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Dehydropolymerization of H₃B·NMeH₂ Using a [Rh(DPEphos)]⁺ Catalyst: The Promoting Effect of NMeH₂

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1. INTRODUCTION

Polynaminoboranes, exemplified by N-methylpolynaminoborane (H₃BNMeH₄)ₙ, have alternating main-chain B–N units and are of interest as precursors to BN-based ceramics or as new exfoliated materials that are isosteres of polyolefins. Since the original report of the synthesis of (H₃BNMeH₄), by the dehydropolymerization of H₃B·NMeH₂ using an Ir(POCP)-H₂ catalyst (POCP = C₃H₃-C₃H₅-C₅H₇-2,6-(OPBu₃)₂), there has been significant progress in developing catalytic methodologies, as well as noncatalyzed routes. The accepted overarching catalytic mechanism operates via initial dehydrogenation of H₃B·NMeH₂ to form a transient free, or metal-bound amine–borane, which then undergoes a head-to-tail BN coupling (Scheme 1). A number of different propagation scenarios have been proposed for this latter step that show elements of chain-growth, step-growth, or hybrid mechanisms. Particularly interesting would be systems that demonstrate the potential for control over the polymerization process, holistically defined by degree of polymerization (as measured by Mₙ), dispersity (D), initiation/termination events, and catalyst lifetime (i.e., TON). While aspects of these performance criteria have been noted, there is no general approach to their optimization.

We have reported cationic dehydropolymerization precatalysts based upon {Rh(Xantphos·R)}⁺ motifs, in which the identity of the PR₃ group is changed (Scheme 2). When R = Ph (A), medium molecular weight polymer is formed (Mₙ = 22 700 g/mol, D = 2.1), a higher catalyst loading promotes lower Mₙ, and H₂ acts to modify the polymer chain length (Mₙ).

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Scheme 2. Comparison of Previously Reported Rh–Xantphos-Based Catalysts and Their Performance in Dehydropolymerization of H₂B-NMe₂H₂. \[\text{BAR}^\text{F}_4\]− Anions Not Shown

\[\text{Rh(Xantphos-Ph)}^+ \text{Precatalyst 2a}\]

\[\text{Rh(DPEphos)}^+ \text{Precatalyst 2b}\]

= 2 800 g/mol, \(D = 1.8\)). Although detailed kinetics for H₂B-NMe₂H₂ dehydropolymerization were not reported, these observations were interpreted as signaling a coordination/insetion/chain-growth mechanism in concert with more extensive studies on H₂B-NMe₂H. \(^9\) There is also a significant induction period observed (≈10 min). In contrast, when \(R = \text{Pr}^+\) (B), \(H₂\) and catalyst loading do not significantly change \(M_n\) (9 500 g/mol, \(D = 2.8\)), there is a negligible induction period, and a dual role \(^1,12\) for the organometallic species was proposed in which dehydrogenation/propagation occurs from different metal centers. This mechanistic switch may be influenced by the preferred ligand-coordination modes. \(^21\) Xantphos-Ph is a hemilabile ligand preferring to coordinate \(\text{cis}-\kappa^2\text{-PP}\) and \(\text{mer}-\kappa^3\text{-POP}\), while Xantphos-Pr prefers \(\text{mer}-\kappa^3\text{-POP}\) (Figure S1 compares coordination modes for crystallographically characterized Xantphos-R complexes).

We now report a detailed and systematic study on the dehydropolymerization of H₂B-NMe₂H using a different Rh-POP-based system: [Rh(DPEphos)]\(^+\) [DPEphos = bis(2-(diphenylphosphino)phenyl)ether]. Using this ligand, which favors \(\text{cis}-\kappa^2\text{-PP}\) coordination (Figure S1), significant control over \(M_n\) by both catalyst loading and \(H₂\) is achieved, with \(M_n\) ranging from 5 500 to 40 000 g/mol and \(D = 1.5–1.8\). These studies also reveal the formation of dimers, and the key role of added amine, NMe₂H, in both promoting catalysis and increasing \(M_n\)/lowering \(D\) of the isolated polymer. Finally, combining these observations, the synthesis and evaluation in a simple [Rh(\(\kappa^2\text{-PP-DPEphos})(\text{NMe₂H})\text{₂}]\(^+\) pre-catalyst is reported. This positive influence of added amine is also shown to 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 H₂B-NH₃ by trapping BH₃ formed from B–N bond cleavage, \(^8\) although the influence of amine on the characteristics of the polymer produced were not commented upon.

2. RESULTS AND DISCUSSION

2.1. Precatalyst and Discussion. Precatalyst 2a, [Rh(\(\kappa^2\text{-PP-DPEphos})(\text{NMe₂H})\text{₂}]\(^+\) (\(\text{DPEphos} = \text{bis}(2-(\text{diphenylphosphino})\text{-phenyl})\text{ether}\)), is synthesized from hydroboration of 4-butylenethene (TBE) by H₂B-NMe₂H using the NBD precursor 1a (NBD = norbornadiene), preactivated by \(H₂\) (Scheme 3).

Spectroscopic data for purple 2a are similar to the previously reported Xantphos-Ph derivative, A. \(^22\) In particular, a single environment is observed in the \(^{31}\text{P}(^1\text{H})\) NMR spectrum [\(\delta = 40.0 \text{ ppm, } J(\text{RhP}) = 180 \text{ Hz}\)], the 3-center, 2-electron Rh\(\cdot\)H–B groups are observed at [\(\delta = 5.55 \text{ ppm (2 H) in the } ^1\text{H}\) NMR spectrum, while the \(^{11}\text{B}\) NMR spectrum shows a characteristically downfield-shifted resonance [\(\delta = 33.3 \text{ ppm}\)], 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 H₂B-NMe₂H₂ dehydropolymerization, \(^9\) TBE hydroboration using H₂B-NMe₂, \(^24\) and B–B homocoupling. \(^22\)

2.2. Dehydropolymerization of H₂B-NMe₂H₂: Variation of Conditions. Precatalyst 2a is an effective for dehydropolymerization, and full conversions of H₂B-NMe₂H₂ are obtained even at low loadings under a slow stream of Ar to remove H₂ (e.g., 0.223 M H₂B-NMe₂H₂, 2a = 0.1 mol %, TON = 1000, 6 h). Variation of precatalyst loadings between 0.2 and 1 mol % reveals an inverse relationship between \(M_n\) of the isolated polymer and catalyst loading (Table 1, entries 1–3, and Figure 1A). The resulting \(^{11}\text{B}\) NMR spectra of the reaction mixtures and isolated polymer show the characteristic, \(^2,12\) broad signal at \(\delta = 6 \text{ ppm for (H₂BNNMethyl), and only trace (HBNNMethyl)}\) (Figure S18). The \(^{13}\text{C}(^1\text{H})\) NMR spectra (H₂-THF) show a relatively sharp peak at \(\delta = 35.5 \text{ ppm (NMe)}\). In contrast, at 0.1 mol % catalyst loading, \(M_n\) does not increase compared to 0.2 mol %, and there is significant 1,2-F₂C₆H₄ insoluble polymer that is tetrahydrofuran (THF)-soluble. NMR spectroscopic analysis of this material (Figure S19) showed additional signals at \(\delta(^{13}\text{C}) = 1 \text{ ppm and } \delta(^{13}\text{C}(^1\text{H})) = 35.7 \text{ ppm (br, NMe)}\) that may signal tertiary or quaternary main-chain centers, suggesting cross-linking/chain branching. \(^10,11,19,25\) 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, vide infra) may have a disproportionate effect on the polymerization process, leading to a different product being formed. When dehydropolymerization was conducted under H₂ measurement conditions (eudiometer, H₂ established in the head space), or in a closed system that allows for H₂ buildup, H₂ likely acts as a chain-transfer/termination agent and significantly shorter polymer is isolated, for which a significantly larger signal at \(\delta(^{13}\text{B}) \approx 18 \text{ ppm is observed}, which could be assigned to BH₃ end groups\) (Figure 1B; Figure S20 shows a representative \(^{11}\text{B}\) NMR spectrum). Similar \(D\) are retained compared with the open system, as is the inverse relationship between \(M_n\) and catalyst loading (Table 1, entries 5–8). Interestingly, there is now a significant difference in \(M_n\) between 0.1 and 0.2 mol %, suggesting that \(H₂\) modifies the influence of the very low catalyst loading. A conversion versus \(M_n\) study (0.2 mol %, open system, Figure 1C) indicates that a chain-growth mechanism is operating, because at low (10%) conversions long polymer chains are observed (\(M_n = 24 800 \text{ g/mol, } D = 1.2\) and H₂B-NMe₂H₂ monomer dominates (Figure S21).

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 an amine–borane and promotes propagation. \(^7\) 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...
The inverse relationship between $M_e$ and catalyst loading suggests dehdropolymerization at a single metal center, as lower catalyst loadings lead to less propagating sites for the concomitantly formed H$_2$B=NMMe. Interestingly, this relationship between $M_e$ and initiating sites is also reminiscent of a classical radical polymerization mechanism where the net order in initiator is negative, as has been recently noted.  

2.3. Speciation Experiments: The Formation of Dimeric Rh$_2$ 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 (0.1–1 mol %) meant that these speciation studies were performed instead at 10 mol % 2a to obtain good signal/noise (sealed NMR tube, 1,2-F$_2$C$_6$H$_4$). Under these in situ conditions, $^{1}H$ NMR spectroscopy showed the formation of a mixture of (H$_2$BNMeH)$_2$ and (H$_2$B)$_2$ (νH(NMMe)) [ν, δ = −22.3 ppm$^{58}$], with the latter potentially signaling free BH$_2$ by loss of amine. $^{3}P$($^1H$) NMR spectroscopy under these conditions showed the initial formation, after 5 min, of two new dimeric complexes: a bridging hydrido-aminoborane 3a, [Rh$_2$(DPEphos)$_2$($μ$-H($μ$-H$_2$B=NMMe))] [ν, δ = −7.1 ppm, $J(BH) = 110$ Hz, cf. authentic sample $J(BH) = 107$ Hz, cf. authentic sample], and an amidodiboryl 4a, [Rh$_2$(κ$^2$-P,P-DPEphos)$_2$($μ$H($μ$-H$_2$B=NMMe))] [ν, δ = −7.1 ppm, $J(BH) = 110$ Hz, cf. authentic sample $J(BH) = 107$ Hz, cf. authentic sample], which comes from a slow fraction were frustrated to form a metal hydride and free H$_2$. Boronium [BH$_2$NMeH]$_2$+ for which subsequent protonation and initiating sites is also reminiscent of the formation of analogous complexes with [Rh$_2$(R$_p$-CH$_2$)$_2$PR$_2$]$_2$($μ$H($μ$-H$_2$B=NR$_2$))$^{13}$ motifs. $^{31,32}$ Here, attack of free amine (from B=N bond cleavage$^{59}$) at a precursor σ-amine–borane complex generates a neutral dimeric Rh–hydride and [BH$_2$NMeH]$_2$+ for which subsequent proton transfer and NMe$_2$ loss result in the bridging amino–borane motif. NMR and ES–MS data for 3a are fully consistent with its formulation (Supporting Materials) and are very closely related to previously reported [Rh$_2$(Pr$_3$P(CH$_2$)$_2$Pr$_3$)$_2$($μ$H($μ$-H$_2$B=NMMe))] [ν, δ = −7.1 ppm, $J(BH) = 110$ Hz, cf. authentic sample $J(BH) = 107$ Hz, cf. authentic sample], and an amidodiboryl 4a, [Rh$_2$(κ$^2$-P,P-DPEphos)$_2$($μ$H($μ$-H$_2$B=NMMe))] [ν, δ = −7.1 ppm, $J(BH) = 110$ Hz, cf. authentic sample $J(BH) = 107$ Hz, cf. authentic sample], which comes from a slow days) recrystallization of 3b, formed in situ from [Rh($κ^2$-P,P-

Table 1. GPC Characterization Data for Isolated Polyaminoborane$^a$

| entry | catalyst | $[\text{Rh}]_{\text{TOT}}$ mol % | conditions | $M_n$ g/mol | D |
|-------|----------|=================|------------|-------------|---|
| 1     | 2a       | 1                | open (Ar flow) | 6400 | 1.8 |
| 2     | 2a       | 0.4              | open (Ar flow) | 29500 | 1.8 |
| 3     | 2a       | 0.2              | open (Ar flow) | 34900 | 1.5 |
| 4     | 2a       | 0.1              | open (Ar flow) | 34600 | 1.7 |
| 5     | 2a       | 0.1              | H$_2$ measurement | 29400 | 1.6 |
| 6     | 2a       | 0.2              | H$_2$ measurement | 14500 | 1.7 |
| 7     | 2a       | 0.4              | H$_2$ measurement | 10100 | 1.8 |
| 8     | 2a       | 1                | H$_2$ measurement | 5500 | 1.8 |
| 9     | 3a       | 0.4              | H$_2$ measurement | 14800 | 1.6 |
| 10    | 4b       | 0.4              | H$_2$ measurement | 15900 | 1.8 |
| 11    | 2a       | 0.4              | H$_2$ measurement/1 equiv of H$_2$B-THF/50 μL of THF | 6600 | 1.9 |
| 12    | 2a       | 0.4              | H$_2$ measurement/10 equiv of H$_2$B-THF/50 μL of THF | 2800 | 2.3 |
| 13    | 2a       | 0.4              | H$_2$ measurement/50 μL of THF | 11000 | 1.6 |
| 14    | 2a       | 0.4              | H$_2$ measurement/~2 equiv of NMeH$_2$ in 50 μL of THF | 27400 | 1.6 |
| 15    | 2a       | 0.4              | open/~2 equiv of NMeH$_2$ in 50 μL of THF | 32100 | 1.6 |
| 16    | S/6      | 0.2              | H$_2$ measurement | 38900 | 1.6 |
| 17    | S/6      | 0.4              | H$_2$ measurement | 33200 | 1.6 |
| 18    | S/6      | 1                | H$_2$ measurement | 20600 | 1.5 |
| 19    | 6        | 0.8              | H$_2$ measurement | 22500 | 1.5 |
| 20    | 2a       | 0.2              | H$_2$ measurement/~2 equiv of NMeH$_2$ in 50 μL of THF | 34800 | 1.5 |
| 21    | A$^a$    | 0.2              | H$_2$ measurement | 40500 | 1.7 |
| 22    | A$^a$    | 0.2              | H$_2$ measurement/~2 equiv of NMeH$_2$ in 50 μL of THF | 61900 | 1.6 |
| 23    | C$^{16}$ | 0.2              | H$_2$ measurement | 63100 | 1.7 |
| 24    | C$^{16}$ | 0.2              | H$_2$ measurement/~2 equiv of NMeH$_2$ in 50 μL of THF | 78900 | 1.6 |

$^a$All at 298 K, 0.223 M H$_2$B-NMeH$_2$, 1,2-F$_2$C$_6$H$_4$ solvent. GPC data quoted relative to polystyrene standards (calibrated between 500 and 480 000 g/mol), triple column, RI detection, THF with 0.1 w/w% [NBU$_4$]Br, 35 °C, sample concentration = 2 mg/cm$^3$. Open conditions: periodic sampling by $^{1}H$ NMR spectroscopy determined end point (e.g., 6 h for entry 4). Under H$_2$ measurement conditions, the reaction was stopped when there was no significant change in $M_n$. from chain-termination/transfer by hydrogenolysis of a Rh=H$_2$(polymeryl) or Rh=NMMeH(polymeryl) bond. The use of H$_2$ as a chain-termination agent in olefin polymerization is well-established, operating through sigma-bond metathesis of [M]-CH$_2$-polymeryl with H$_2$ to form a metal hydride and free polymer.$^{26}$ The inverse relationship between $M_e$ and catalyst loading suggests dehdropolymerization at a single metal center, as lower catalyst loadings lead to less propagating sites for the concomitantly formed H$_2$B=NMMeH. Interestingly, this relationship between $M_e$ and initiating sites is also reminiscent of a classical radical polymerization mechanism where the net order in initiator is negative,$^{27}$ as has been recently noted.  

Figure 1. GPC data (relative to polystyrene standards, RI detection, THF with 0.1 w/w% [NBU$_4$]Br, 35 °C) for (H$_2$BNMeH)$_2$, isolated from H$_2$B-NMeH$_2$ dehdropolymerization (0.223 M, 1,2-F$_2$C$_6$H$_4$, 20 °C) using catalyst 2a. (A) Variation of [2a] under Ar purge; (B) variation of [2a] under H$_2$ measurement conditions (eudiometer); (C) conversion versus $M_e$/D plot, open conditions, where each individual data point is a PPh$_3$-quenched experiment after an appropriate time.
The Research Article have been H or amino α9 NMR spectrum. two α centers [e.g., Rh2−NMR spectrum [e.g., and cis to the Rh bond, while P1 and P4 lie trans to the BH agostic interaction MS), and the description results in formally Rh(II) centers with a Rh−Rh bond, 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/B2−H, 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 center are also observed in the \( \text{QTAI} \)M analysis and also observed experimentally, e.g., Rh1···C38, 2.997(5) Å. Consistent with such interactions, a broad asymmetric signal is observed at \( \delta = 3.94 \text{ ppm (2 H)} \) in the \(^1{H} \) NMR spectrum of 4b that is attributed to agostic Rh−H/C_{phenyl} interactions, similar to that observed in [Ru(PP3)2(H)(C_{6}H_{5}C_{6}H_{5}N)]−[Ba_{2}A_{4}] (\( \delta = 4.14 \text{ ppm} \)). 3b 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−α-BH···Rh agostic,39 or amino−boryl motifs40 have been reported before. However, as far as we are aware, the amido−bisboryl structure is a new motif in metalloborane chemistry. Perhaps most closely related to 4b is a Rh-δimer with P−C activated Xanthos-Ph ligands and a bridging N,N-dimethylaminodiboranate unit ([H_{3}NMe_{3}H_{2}B_{2}H_{6}]) that is isolated at the end of dehydrocoupling of H_{3}B_{2}Me_{2}H when using catalyst A. Interestingly, this is also a competent catalyst for H_{3}B_{2}Me_{2}H dehydropolymerization.20 While we currently can only speculate on the mechanism of formation of 4, it is connected to 3 by simple addition of BH and very little N-trimethylborazine was observed by \( ^{11} \text{B} \) NMR spectroscopy (<5%, Figure S23), indicating that evolved H_{2} is a good proxy for transient H_{2}B≡NMeH equivalents formed

Figure 2. (A) Addition of H_{2}B-NMeH_{2} to 2a (10 mol %) to form 3a and 4a, 1,2-F_{2}C_{6}H_{4} solvent. (B) Synthesis and solid-state structure of the cationic portion of 4. Selected bond lengths (Å) and angles (deg): 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 2.997(5); B1−N1 1.59(1); B2−N1 1.56(1); P1−Rh1−Rh2 162.59(3), P2−Rh1−Rh2, 95.31(3).

Figure 3. Contour plot of the electron density of the central cationic portion of 4b presented in the \{Rh_{2}N{^3}Rh\} plane with projected stationary points, bond paths, bond critical points (BCPs; green), and ring critical points (RCPs; red). The associated table shows selected BCP metrics (a.u.; average data for indicated bonds).
and subsequent polymer chain growth. A significant induction period was observed prior to faster turnover (e.g., ∼60 min, 0.4 mol %), that gets longer with increase in [2a]₀ (Figures 4A and S24; e.g., 0.1 mol %, tᵢₘₐₓ = 33 min; 1 mol %, tᵢₘₐₓ = 110 min). An induction period has also been noted for catalyst A in H₂B-NMeH₃ dehydropolymerization as well as for [Rh(Ph₃P)(CH₂)₅PPh₃)(FC₇H₄)][BF₄] with in H₂B-NMeH-dehydrocoupling (10 and 5 min, respectively, at 0.2 mol %). For this latter system, increased [Rh]ᵢₜₒᵗₜₒₜ also led to longer induction periods, and a subsequent study showed the initial formation of an amino–borane-bridged dimer analogous to 3a. While the observation of an induction period might suggest a heterogeneous system here, adduction of excess Hg or stoichiometric PPh₃, during productive turnover did not significantly reduce reaction rate, and no darkening of the reaction was noted, pointing toward homogeneous catalysis (Figure S25). Overall, the kinetics evolve in a sinusoidal manner, with a rate maximum reached approximately at the midpoint (e.g., 0.4 mol %, tᵢₘₐₓ = 4.1(2) × 10⁻⁷ M⁻¹ s⁻¹). This behavior is suggestive of a long induction period coupled to rate-attenuation as the substrate is depleted. There is a noninteger dependence of the maximum rate on the initial catalyst concentration (Figure S28), which hints at more complex kinetics. Using 0.223 M D₅B-NMeH₃ or H₂B-NMeD₂ at 0.4 mol % 2a, kinetic isotope effects (KIEs) determined from νₘₐₓ were k(BH)/k(BD) = 1.1 ± 0.1 and k(NH)/k(ND) = 2.2 ± 0.1, which suggests that 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 approximately the same Mₙ at a similar rate for second recharge (Figure S31). 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 min, 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, H₂ evolution (a proxy for H₂B=NMeH formation) followed a first-order profile (Figure 4B, kₒₜₒₜₒₜ = 3.2(1) × 10⁻⁴ s⁻¹), and this allowed for a half-order dependence on initial catalyst concentration, i.e., [Rh]ᵢₜₒᵗₜₒₜ to be estimated (Figures 4C and S30).

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]ᵢₜₒᵗₜₒₜ (Table 1, entries 7, 9, and 10). Speciation studies at 1 mol % 2a return only 3a at the end, which suggests that, if formed, 4a must be consumed under the conditions of catalysis. Overall these data show the following: a change in H₂-evolution kinetics on moving from 2a (complex) to 4 (pseudo-first-order), that 4 likely sits 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]ᵢₜₒᵗₜₒₜ when using 4a as a precatalyst suggests a lower-order (ligation or nuclearity) active catalyst that is in a rapid equilibrium with a higher-order inactive 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 1 equiv of H₂B-THF (in 50 μL of THF) to 0.4 mol % [2a]/H₂B-NMeH₁/1.2-F₅-C₅H₄ solvent increased the induction period significantly (Figure 4A) and gave significantly shorter polymer (Table 1, entry 11), while 10 equiv halts catalysis, possibly by the formation of inactive boron-rich species (see Supporting Information). Added [H₂B(NMeH₂)₂][BF₄] (10 equiv) significantly slows catalysis, now taking 24 h 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, in particular the [Rh-(XanthoPr)₂]⁺ system, where it promotes catalysis. At low relative concentrations, H₂B-THF presumably acts to titrate out NMeH₂, while we propose that excess [H₂B(NMeH₂)₂]⁺ acts to poison catalysis, possibly sequestering NMeH₂ via N–H–NMeH₂ hydrogen bonding, as noted for related bis(phosphine)boronium salts. The control experiment of THF addition (50 μL) reduced the induction period to 30 min and produced polymer comparable to nondoped experiments (Table 1, entry 13). The most dramatic change came from addition of ∼2 equiv of NMeH₂ (in 50 μL of THF) to 0.4 mol % [2a]/H₂B-NMeH₂. This resulted in a kinetic profile for H₂ evolution that now showed no induction period and pseudofirst-order kinetics for hydrogen evolution (kₒₜₒₜₒₜ = 3.7(1) × 10⁻⁴ s⁻¹), similar to that of 4b at the same [Rh]ᵢₜₒₜₒₜ. 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 nondoped experiments (cf. entries 14/15 and 2/7, Table 1). These observations, alongside the speciation data at 10 mol %, which 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 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 in situ by
addition of amine to the precatalyst, 2a. Addition of ~2 equiv of NMeH₂ (in THF) to 2a gave the simple bisamine complex [Rh(k²-P,P-DPEphos)(NMeH₂)₂][BAR₄], 6, which reacts rapidly (on time of mixing) with H₂ in situ to form the corresponding dihydride [Rh(k²-P,P-DPEphos)-
(H)₂(NMeH₂)₂][BAR₄], 5 (Scheme 4). Complex 5 reversibly,

but slowly, loses H₂ under extended degassing to reform complex 6, and thus we suggest that, 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/2a × NMeH₂/H₂/degas and used directly in catalysis (see Supporting Information). Complex 5 is the sole organometallic product on addition of ~2 equiv of NMeH₂ to a 1:3 mixture of 3a/4a, alongside H[B(NMeH)₂] [δ(H)B] 28.6 ppm, [δ(BH) = 127 Hz], demonstrating the role of NMeH₂ in both generating 3, via boronium formation, and bringing dimeric 3 and 4 back to monomeric species. Complex 6 (and 5 on subsequent addition of H₂ in solution) can be prepared as a free-flowing pure solid in bulk via an alternative route, from addition of NMeH₂ to [Rh(k²-P,P-DPEphos)(η⁶-o- MeC₆H₄)][BAR₄], 7, which enables definitive characterization by NMR spectroscopy. However, this involves laborious multiple triturations with cold pentane, and thus, the in situ prepared mixture is more convenient to use. Notable NMR spectroscopic data for 6 are the observation of equivalent NMeH₂ groups in the H NMR spectrum, while for 5 addition of H₂ makes these groups 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 phosphorus environments are observed in the 3¹P[¹H] NMR spectrum (Supporting Information). Data from H₂-evolution kinetics and isolated polymer using isolated 6 fit well with the trends apparent from using the 5/6 in situ mixture (Table 1 and Figure 5).

Using in situ generated 5/6 gave pseudo first-order plots for H₂ evolution (e.g., 0.4 mol %, kobs = 4.1(1) × 10⁻⁴ s⁻¹) with no induction period observed. 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 turnover-limiting step, in which the higher nuclearity species is inactive but dominant, or the rapid and reversible dissociation of a ligand that reveals a low concentration of an active species. Monomer/dimer equilibria have been proposed in polymerization systems previously, and in amine–borane dehydrocoupling specifically. While addition of 10 equiv of NMeH₂ caused no significant change in rate (kobs = 4.2(1) × 10⁻⁴ s⁻¹), suggesting that NMeH₂ dissociation is not occurring, the polymer isolated from this experiment was insoluble in THF. We thus cannot rule out a change in mechanism. We discount rapid and reversible H₂ loss as the reason for the observed half-order kinetics because under conditions of measurement H₂ effectively becomes saturated and constant. Speciation studies with excess NMeH₂ (10 equiv, [Rh] TOTAL = 5 mol %) revealed 5 to be the only observed organometallic species. No significant change in kinetics was observed on addition of excess H₂ or 0.2 equiv of PPh₃ during catalysis—suggesting a homogeneous system. The use of these in situ prepared amine complexes 5/6 leads to polymer with greater Mₙ (but still inverse with regard to [Rh] TOTAL), while D is kept relatively low (Figure 5B, e.g., 1 mol %, Mₙ = 20 600 g/mol, 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.

Following catalysis by 3¹P[¹H] NMR spectroscopy using pure 5 (1 mol %) showed that during productive catalysis a single organometallic species is observed (albeit with low signal-to-noise) as a doublet at δ 41 ppm [J(RhP) = 150 Hz], which slowly resolves to complex 3 at the end of catalysis. Importantly, the same species is observed when starting with precatalyst 4b (0.5 mol %, 1 mol % [Rh] TOTAL). This strongly suggests that both precatalysts evolve to a common species—the identity of which remains to be resolved.

Interestingly, the promoting effect of NMeH₂ is not operative in the [Rh(Xantphos·Pr)(H)]⁺ system, which 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·κ⁴-POP·Xantphos·Pr)(H)₂(NMeH₂)][BAR₄], 8 (see Supporting Information), does not dehydropolymerize H₂B-NMeH₂ returning unchanged substrate after 1 h (0.2 mol %, 0.111 M H₂B-NMeH₂). This is probably due to the relatively strongly bound amine blocking access of H₂B-NMeH₂ to the metal center, at which the Xantphos·Pr is also not hemilabile (Figure S1), so that σ-complex formation by coordination of amine–borane, and subsequent dehydrogenation by BH/NH activation, does not take place. The broader promoting effects of NMeH₂ are, however, evident in other cationic {Rh(chelating phosphine)}⁺ systems that are suggested to undergo a coordination/dehydrogenation/chain-growth mechanism. Under the specific conditions reported here, both [Rh(Xantphos·Ph)]⁺, 9, and [Rh(Ph₃P-
Table 2. Effect of Added Amine in Selected Cationic Rh Catalysts, $M_a$ (g/mol) and $D_1$ 0.223 M, 0.2 mol % Catalyst, H$_2$ Measurement Conditions, 1,2-F$_6$C$_6$H$_{14}$; [BAR$_4^{2-}$] Anions Not Shown

| catalyst | no added amine | ~2 equiv of NMeH$_2$ |
|----------|----------------|---------------------|
| [Rh(DPPhos){H$_2$B(NMe$_2$)(CH$_2$)$_3$/Bu}]+ 2a | 14500 (1.7) | 34800 (1.5) |
| [Rh(Xantphos-Ph){H$_2$B(NMe$_2$)(CH$_2$)$_3$/Bu}]+ A | 40500 (1.7) | 60900 (1.6) |
| [Rh(PH$_3$P(CH$_2$)$_3$/PPh$_3$){C$_6$H$_3$F}]+ C | 61300 (1.7) | 78900 (1.6) |

(Ch$_2$I$_2$/PPh$_3$), Ch$_3$. systems show increased $M_a$ slightly lower $D_1$ and no induction periods when ~2 equiv of NMeH$_2$ is added to the precatalyst, compared to the nondoped controls (Table 2).

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

Scheme 5. Pathways for Catalyst Activation and Catalysis in the Dehydropolymerization of H$_2$B-NMeH$_2$ Using [Rh] = {Rh(DPPhos)}$^+$ Precatalysts

that gets longer with increased [2a] can also now be explained. NMeH$_2$ generated by slow B–N bond cleavage of H$_2$B-NMeH$_2$ at a rate that is independent of [2a], first promotes the formation of 3a and then more slowly the active precatalyst 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 NMeH$_2$ 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 NMeH$_2$ suggests this does not reversibly dissociate, while a sensible model in which dimeric 4a, with its Rh–Rh bond and bridging amido–bisseryl ligand, undergoes rapid and reversible dissociation (vide supra) or loss of ligand is not obvious. Moreover, 4b reacts rapidly with NMeH$_2$ to form 5, suggesting that if formed in catalysis it is not persistent. In addition, the fact that both 5 and 4b evolved to the same, currently unresolved, organometallic species under catalytic conditions suggests that both sit just outside of the productive catalytic cycle. 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 $[\text{Rh}]_{\text{TOTAL}}$ and the observation of dimeric species (3 and 4) suggest that such Rh$_2$ motifs may be intimately involved. The strong, and persistent, inverse relationship between $M_a$ and $[\text{Rh}]_{\text{TOTAL}}$ coupled with the sensitivity to H$_2$, suggests a coordination/insertion/chain-growth mechanism for which NMeH$_2$ also modifies chain length—possibly by attenuating chain termination. On the basis of the half-order kinetics observed from the dehydrogenation studies, we suggest three possible general motifs for the active catalytic (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 Rh$_2$ hydride dimers that can form in Rh-catalyzed alkene hydrogenations, while scenario B is supported by the recent report that dimeric early transition-metal complexes have been shown to act as competent catalysts for H$_2$B-NMeH$_2$ dehydropolymerization. A third possibility is that deprotonation of bound NMeH$_2$ provides an active Rh–NMeH amido motif, similar to the bifunctional catalysts developed by Schneider and co-workers (C).

Scheme 6. Generalized Possible Active Species in Catalysis

$^a$P = phosphine, L = ligand (e.g., NMeH$_2$, 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 NMeH$_2$ can be used to control the dehydropolymerization of H$_2$B-NMeH$_2$ in a {Rh(DPPhos)}$^+$-based catalyst. We proposed 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. The ability to control polymerization by catalyst loading, NMeH$_2$ addition, and H$_2$ in {Rh(DPPhos)}$^+$ and {Rh(Xantphos-Ph)}$^+$ systems is markedly different from that found for the {Rh(Xantphos-Pr)}$^+$ 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: DPPhos and Xantphos-Ph prefer cis-k$_2$-P,P, while Xantphos-Pr generally adopts mer-k$_3$-P,O,P motifs. The 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{1,3} dehydropolymerization catalysts from across the transition metals.

**ASSOCIATED CONTENT**

\textsuperscript{1} Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b00081.

Full experimental section, characterization details, kinetic data and details of the DFT calculated structure, and QTAIM analysis of 4b (PDF)

Crystallographic data (CIF)

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**Notes**

The authors declare no competing financial interest.

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