Mechanistic Studies of the Dehydrocoupling and Dehydropolymerization of Amine–Boranes Using a [Rh(Xantphos)]⁺ Catalyst

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ABSTRACT: A detailed catalytic, stoichiometric, and mechanistic study on the dehydrocoupling of H₃B·NMεMe₂H and dehydropolymerization of H₃B·NMεMe₂H using the [Rh(Xantphos)]⁺ fragment is reported. At 0.2 mol % catalyst loadings, dehydrocoupling produces dimeric [H₂B·NMεMe₂] and poly(methylaminoborane) (Mₙ = 22 700 g mol⁻¹, PDI = 2.1), respectively. The stoichiometric and catalytic kinetic data obtained suggest that similar mechanisms operate for both substrates, in which a key feature is an induction period that generates the active catalyst, proposed to be a Rh–amido–borane, that reversibly binds additional amine–borane so that saturation kinetics (Michaelis–Menten type steady-state approximation) operate during catalysis. B–N bond formation (with H₂B·NMεMe₂H) or elimination of amino–borane (with H₂B·NMεMe₂H) follows, in which N–H activation is proposed to be turnover limiting (KIE = 2.1 ± 0.2), with suggested mechanisms that only differ in that B–N bond formation (and the resulting propagation of a polymer chain) is favored for H₂B·NMεMe₂H but not H₂B·NMεMe₂H. Importantly, for the dehydropolymerization of H₂B·NMεMe₂H, polymer formation follows a chain growth process from the metal (relatively high degrees of polymerization at low conversions, increased catalyst loadings lead to lower-molecular-weight polymer), which is not living, and control of polymer molecular weight can be also achieved by using H₂ (Mₙ = 2 800 g mol⁻¹, PDI = 1.8) or THF solvent (Mₙ = 52 200 g mol⁻¹, PDI = 1.4). Hydrogen is suggested to act as a chain transfer agent in a similar way to the polymerization of ethene, leading to low-molecular-weight polymer, while THF acts to attenuate chain transfer and accordingly longer polymer chains are formed. In situ studies on the likely active species present data that support a Rh–amido–borane intermediate as the active catalyst. An alternative Rh(III) hydrido–boryl complex, which has been independently synthesized and structurally characterized, is discounted as an intermediate by kinetic studies. A mechanism for dehydropolymerization is suggested in which the putative amido–borane species dehydrogenates an additional H₂B·NMεMe₂H to form the “real monomer” amino–borane H₂B·NMεH that undergoes insertion into the Rh–amido bond to propagate the growing polymer chain from the metal. Such a process is directly analogous to the chain growth mechanism for single-site olefin polymerization.

1. INTRODUCTION

Catalytic routes for the formation of main-group/main-group bonds are important for the targeted construction of new molecules and materials. However, enabling catalytic methodologies for such bond-forming events lag behind those developed for the construction of C–C and C–X bonds. The development of reliable, robust, and controllable processes is thus an important challenge. Catalytic dehydropolymerization of amine–boranes to give polyaminoboranes presents one such opportunity, as this produces new BN polymeric materials that are isoelectronic with technologically pervasive polyolefins. Such new materials have potential applications as high-performance polymers and as precursors to BN-based ceramics and single-layer hexagonal BN thin films (white graphene). Although ill-defined branched, oligomeric materials that have been termed “polyaminoborane” have historically been prepared by noncatalytic methods, it is only recently that high-molecular-weight, essentially linear polyaminoboranes have been produced by catalytic methods from amine–boranes such as H₂B·NH₃ and H₂B·NMεMe₂H (Scheme 1), initially using Brookhart’s catalyst Ir(BuPOCOP’Bu)H₂ [BuPOCOP’Bu = k²-PCP-1,3-(OP’Bu₂)₂C₄H₄]². In 2006, Goldberg, Heinkey, and co-workers demonstrated that H₂B·NH₃ could be dehydrodimerized using this Ir catalyst to afford an insoluble material tentatively reported as...
Scheme 1. Dehydropolymerization of Amine–Boranes Using the Ir(‘BuPOCOP’Bu)H2 Catalyst

\[ \text{Scheme 2. Suggested Pathways for Dehydropolymerization, Dehydrogenation, and Hydroboration}\]

\[ \text{On-Metal Dehydrocoupling} \]

\[ \text{Off-Metal Dehydrocoupling} \]

\[ \text{adapted from ref 37.} \]
hydrogen redistribution reactions can also occur, in which amino−boranes take part in hydrogen transfer with amine−boranes, while a nucleophilic solvent (e.g., THF) can also potentially catalyze polyaminoborane formation from amino−boranes. Mechanistic insight that comes from the direct observation of intermediates in dehydropolymerization is also very rare, although off-cycle products have been reported. The product of the first insertion event of H3B·NMeH2 using the [Ir(PCy3)2(H)2]+ fragment has been shown to be [Ir- (PCy3)2(H)2(η2-H3B·NMeHBH2·NMeH2)][BARF4] (ArF = 3,5-(CF3)2C6H3), in which the resulting diborazane forms a σ complex with the Ir center (Scheme 3a). Studies on closely related phospine−borane dehydrocoupling using the [Rh(Ph3P(CH2)3PPh2)]+ fragment, which is also an excellent catalyst for amine−borane dehydropolymerization, provide complementary insight, and intermediates that sit each side of the dehydrocoupling step have been characterized, allowing for activation parameters for the P−B bond forming event to be determined (Scheme 3b). These intermediates show that P−H activation has occurred to give a Rh(III) phosphino hydride with supporting intra- and intermolecular σ (B−H···Rh) interactions. By using the [Rh(Xantphos)]+ fragment (Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene), which is valence isoelectronic to [Ir- (tBuPOCOP)Bu], B−B homocoupling of H3B·NMe3 gives a diborane(4) complex (Scheme 3c). Computation and experiment point to a pathway in which a low energy reversible B−H activation of amine−borane is followed by a second, higher energy B−H activation and B−B coupling, with these steps being related to those generally invoked in B−N bond formation in dehydropolymerization.

Encouraged by the ability of the [Rh(Xantphos)]+ fragment to B−B homocouple amine−boranes, we now report its use in a detailed stoichiometric, catalytic, and mechanistic/kinetic investigation into the dehydropolymerization of H3B·NMeH2 to form polyaminoborane. Additional mechanistic and structural data on the processes occurring comes from the reactions of this fragment with H3B·NMe3, H2B·N3iPr2, and H3B·NMe2H. These studies lead to an overall mechanistic framework for dehydropolymerization using transition-metal fragments that supports and adds to the dehydrogenation/coordination/insertion mechanism proposed by others. This insight leads to the gross control of the degree of dehydropolymerization, allowing for both low- and higher-molecular-weight polyaminoboranes to be obtained.

2. RESULTS

2.1. Stoichiometric Reactivity of Precatalyst [Rh(η4−Xantphos)[η2-H3B(NMe3)CH2CH2Bu]][BARF4]. The stoichiometric reactivity of the [Rh(Xantphos)]+ fragment with amine−boranes is described first, as this provides baseline reactivity with which to contextualize subsequent
**Scheme 5. Reactivity of 2**

"[BARF₄]⁻" anions are not shown. 1,2-F₂C₆H₄ is the solvent.

**Scheme 6. Dehydrocoupling of H₃B·NMe₂·H**

"[BARF₄]⁻" anions are not shown. C₆H₂F is the solvent.
concomitant transfer of H2 to Rh. Complex 5 is not stable and is slowly consumed, so that after 5 h, the Rh(III) dihydride \( [\text{Rh}(\kappa^2\text{POC-Xantphos})(\text{H})_2(\eta^1\text{H}_2\text{B}[\text{NMMe}_3]\text{CH}_2\text{CH}_2\text{Bu}]) \cdot \text{BARF}_2 \) is formed alongside \([\text{H}_2\text{B}−\text{NMMe}_2\text{H}]_2\) (Scheme 6). Complex 6 has been spectroscopically characterized (see the Supporting Information) and shows very similar data to 2 and 5 but now has the borane I bound to the metal center. Complex 6 presumably forms after dehydrogenation of 5 (and release of H2) in the absence of excess H3B-NMMe. Interestingly 1 and 6 are shown to be in equilibrium with one another, as addition of H2 (4 atm) to 1 results in a 3:1 mixture of 6 to 1, which is biased back in favor of 1 on removal of H2. However, we discount a significant role for the equilibrium between 6 and 1 during catalysis, based on the following observations: (i) 1 rapidly reacts with H2-B-NMMe to form 5; (ii) 6 only forms slowly at low H2-B-NMMe concentration from 5; (iii) the temporal evolution of catalysis is the same whether starting from Rh(I) or Rh(III) precursors; and (iv) excess I does not change the observed temporal profile of catalysis (vide infra). This is contrast to the autocatalytic role that the final product \([\text{H}_2\text{B}−\text{NMMe}_2\text{H}]_2\) has been shown to take in dehydrocoupling of H2-B-NMMe as catalyzed by the \([\text{Rh}(\text{PCy}_3)_2](\text{H})_2]_+\) fragment.27 Addition of D2 to 5/H2-B-NMMe results in H/D exchange at the B−H and Rh−H positions as well as in the free amine−borane (as measured by 2H NMR spectroscopy) indicating that reversible B−H activation is a relatively low energy process. No H/D exchange was observed at nitrogen (by 2H NMR spectroscopy), suggesting that reversible N−H activation is considerably higher in energy, as has been noted before in related systems.66,67 Slow dehydrogenation of H2-B-NMMe is also observed.

2.1.3. H3B−NMMeH. Addition of 2 equiv of H3B−NMMe to 1 resulted in the immediate formation of the Rh(III) dihydride complex \([\text{Rh}(\kappa^2\text{POC-Xantphos})(\text{H})_2(\eta^1\text{H}_2\text{B}−\text{NMMeH})][\text{BARF}_2\text{]}_2\), 7 (Scheme 7). Complex 7 was characterized by NMR spectroscopy, and these data are very similar to those for 2, 5, and 6. The amino−borane that would arise from initial dehydrogenation, H3B=NMMeH, was not observed;38 however, the ultimate thermodynamic product of dehydrocoupling, N-trimethylborazine, III, was formed (δ(B) 33.3, doublet; lit. 33.2).39 There was no evidence for the formation of polymeric BN materials or the potential cyclic trimborazine intermediate, \([\text{H}_2\text{BNMeH}]_2\).69 We have recently90 shown that when the amino−borane H3B=NM for release from a metal center it undergoes trimerization to form \([\text{HBN} \text{Bu}_3]_2\) by an (unresolved) mechanism in which hydrogen-redistribution processes are occurring,44 and it is possible that such processes are also operating here. As found for 5, complex 7 undergoes a second, slower dehydrogenation. This process is a little faster than for 5, taking 2 h to fully consume 7 to afford III and an equilibrium mixture of 6/1. Addition of NCMe (excess) to 7 affords the corresponding MeCN adduct, 3, and free H3B-NMMeH.

2.1.4. General Comments on the Stoichiometric Reactivity. These observations show that, under noncatalytic conditions, dehydrogenation of H2-B-NMMeH or H2-B-NMMeH2 at a Rh(I) center (i.e., 1) is rapid, while at a Rh(III) dihydride center (i.e., 5 or 7), it is slower, even though B−H activation (as measured by H/D exchange experiments for H3B-NMMe) is fast at the RhIII center. These observations are similar to those previously reported for the \([\text{Rh}(\text{PR}_3)_2]_+\) and \([\text{Rh}(\text{PR}_3)_2](\text{H})_2]_+\) fragments, respectively.27,51 As will be demonstrated, this slower rate of dehydrogenation of 5 and 7 is in contrast to the fast consumption of H2-B-NMMeH or H2-B-NMMeH2 under catalytic conditions (e.g., 0.2 mol %, 0.072 M H2-B-NMMeH). In addition, under catalytic conditions, H2-B-NMMeH2 is dehydropolymerized to give \([\text{H}_2\text{BNMeH}]_n\), rather than forming trimethylborazine III, and there is an induction period observed before catalysis. These observations suggest additional mechanistic considerations need to be adopted under the conditions of high ratios of amine−borane to metal−ligand fragment, and these are discussed next.

2.2. Catalysis. 2.2.1. Initial Experiments Using H2-B-NMMeH and H2-B-NMMeH2. Under catalytic conditions (0.2 mol %, 0.072 M H2-B-NMMeH, 1,2-Fe,C6H4 as solvent, open system to a slow flow of Ar), complex 1 catalyzes the dehydrogenation of H2-B-NMMeH to ultimately form dimeric II (Scheme 8a). Following this reaction by 11B NMR spectroscopy using periodic sampling of the reaction mixture shows that there was an induction period of approximately 400−500 s, and H2-B=NMMe was also observed as an intermediate during the productive phase of catalysis. Turnover is relatively fast once the induction period is over, with an overall TOF ~1200 h−1 (TOF = 500), which is a rate that is comparable to \([\text{Rh}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2](\eta^6-\text{C}_6\text{H}_4\text{H})(\text{F})][\text{BARF}_2\text{]}_2\),21 which also shows an induction period and is suggested to be homogeneous in character. Very similar temporal profiles are observed starting from the Rh(III) complex 2 (Supporting Information), suggesting that the induction period is not due to the formation of the simple Rh(III) analogue (i.e., 5), consistent with the rapid formation of 5 from 1 (Scheme 6). This also argues against the involvement of 1 during the induction period or catalysis, as 2 is generated without I being present. At ~30% conversion (~<900 s), addition of Hg to the catalyst solution, or filtration of the catalyst mixture through a 0.2 μm filter and addition of a further 500 equiv of H2-B-NMMeH did not result in the termination of catalysis (see the Supporting Information): observations that suggest a homogeneous system.34 The catalyst can also be recycled, in that addition of a further 500 equiv of H2-B-NMMeH to the catalytic mixture directly at the end of catalysis resulted in essentially the same rate and overall turnover number. There is no induction period observed in this recharging experiment or in the filtration experiment, suggesting that the catalyst remains in its active form in both. No significant amount of the linear diborazine H3-B-NMMeBH3-NMMeH268 was observed, similar to \([\text{Rh}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2](\eta^6-\text{C}_6\text{H}_4\text{H})(\text{F})][\text{BARF}_2\text{]}_2\) but different from \([\text{Rh}(\text{PR}_3)_2]_+\) systems where it is observed in significant amounts.27,55,58

In a closed system (New Era high pressure NMR tube), catalysis is significantly slower (Scheme 8b), with TOF ~130 h−1 (TOF = 500). A very similar induction period to the open system is observed, and H2-B=NMe2 is also an intermediate. We27 and others23 have commented previously on the rate inhibition by H2 in amine−borane dehydrocoupling. For example, with the \([\text{Rh}(\text{PCy}_3)_2]_+\) catalyst, H2 buildup forces

![Scheme 7. Borazine Formation at Low [H2-B-NMMeH]2](image-url)
the system to sit in a Rh(III)/Rh(III) cycle that turns over considerably slower than the Rh(I)/Rh(III) cycle. The more active Rh(I) oxidation state is generated by addition of the product II to [Rh(PCy3)2(H)2]+ that promotes H2 reductive elimination, i.e., autocatalysis. In our system, addition of 200 mol % of II prior to catalysis (0.2 mol % I, 0.072 M amine—borane, open system) resulted in no significant change in the reaction profile, consistent with the lack of reaction between I and II under stoichiometric conditions on the time scale of catalysis (Scheme 5). Addition of 55 equiv of I also did not change the catalytic temporal profile (Supporting Information) demonstrating that it does not act to modify catalysis.

Catalyst I also dehydropolymerizes H3B-NMe-H (0.2 mol % I, 0.44 M amine—borane, open system, 2 h, C6H5F as solvent) to afford polyaminoborane [H3B-NMeH]n (Mn = 22 700 g mol−1, PDI = 2.1 using polystyrene standards for GPC column calibration). This is lower molecular weight than typically formed using the [Ir(BuPOCOPBu)H2] catalyst (Mn = 55 200 g mol−1, PDI = 2.9) in THF as solvent.15 The Rh(III) catalyst 2 also produced a very similar polymer to that for I (Mn = 24 800 g mol−1, PDI = 1.9). These polymers formed show 11B NMR spectra very similar to that reported for high-molecular-weight [H3B-NMeH]n produced from [Ir(BuPOCOPBu)H2] and [Rh(Ph2PCH2CH2PPh3)(η5-C6H8)]/[BARF6]21 catalysts, with a broad, symmetrical peak observed at δ −5.4 (fwhm = 720 Hz, Figure 1a).15 No significant signals were observed around δ 0 that might indicate chain branching,23 although such a feature if small could be lost in the peak width of the main signal. To the detection limit of 11B NMR spectroscopy (ca. 5%), no signals were observed between δ 30−40 that could be assigned to free MeHN=BH(R).

A time/conversion plot for H3B-NMe-H dehydrocoupling to form polyaminoborane using catalyst 1 in an open system is shown in Scheme 9 alongside a hydrogen-evolution plot, as measured by gas buret. As for H3B-NMe-H, there is a significant induction period (10 min) before the rapid dehydrocoupling occurs. Polymer formation and hydrogen evolution track one another, and by the end of catalysis (7200 s, 98% conversion, ToF ∼250 h−1), just over 1 equiv of H2 has been produced, consistent with the formation of polyaminoborane of empirical formula approximating to [H3B-NMeH]n. This reaction is considerably slower than for H3B-NMe-H but this might reflect the poorer solubility of H3B-NMeH in C6H5F. Neither trimethylborazine, III, nor signals assignable to free H3B=NMeH were observed during the reaction using 11B NMR spectroscopy when interrogated by regular sampling of the catalysis mixture.

Addition of the linear diborazane H3B-NMeH2-H-NMeH2 to I (20 mol %) in a sealed NMR tube resulted in the formation of N-trimethylborazine III, alongside unidentified metal products. No significant amounts of polyaminoborane or cyclic triborazane [MeHN=HBH2]69 were observed under these near-stoichiometric conditions. However, at 0.4 mol % of I significant amounts of polyaminoborane were observed (Mn = 15 400 g mol−1, Mw = 27 800 g mol−1, PDI = 1.8), so that this is

Scheme 8. 11B Time/Concentration Plots of the Dehydrocoupling of H3B-NMe-H

(a) Open System

(b) Closed System
Scheme 9. Polymer Conversion Plot (Triangles) and H₂ Evolution (Squares, Gas Buret, Calculated at 26 °C) for the Dehydrocoupling of H₂B·NMeH₂.

Table 1. Dehydropolymerization Data, Mₙ by GPC

<table>
<thead>
<tr>
<th>entry</th>
<th>condition</th>
<th>Mₙ (g mol⁻¹)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1, 0.2 mol %</td>
<td>22 700</td>
<td>2.1</td>
</tr>
<tr>
<td>2</td>
<td>2, 0.2 mol %</td>
<td>24 800</td>
<td>1.9</td>
</tr>
<tr>
<td>3</td>
<td>1, 0.4 mol %, 0.22 M, H₂B·NMeHBH₂·NMeH₂</td>
<td>15 400</td>
<td>1.8</td>
</tr>
<tr>
<td>4</td>
<td>1, 0.2 mol %, further 500 equiv</td>
<td>17 900</td>
<td>1.8</td>
</tr>
<tr>
<td>5</td>
<td>1, 1 mol %</td>
<td>10 000</td>
<td>1.5</td>
</tr>
<tr>
<td>6</td>
<td>1, 0.2 mol %, closed</td>
<td>28 800</td>
<td>1.8</td>
</tr>
<tr>
<td>7</td>
<td>1, 0.2 mol %, THF solvent</td>
<td>52 200</td>
<td>1.8</td>
</tr>
<tr>
<td>8</td>
<td>1, 0.2 mol %, excess cyclohexene</td>
<td>38 600</td>
<td>1.8</td>
</tr>
</tbody>
</table>

*100% conversion after first measured point (2 h) as determined by ¹¹B NMR spectroscopy. 0.44 M [H₂B·NMeH₂], open system, C₆H₅F unless otherwise stated. *Greater than 95% conversion, 24 h. *85% conversion, 19 h.

for polymer conversion, each point is a separate experiment in C₆H₅F, with the product precipitated with hexane. The conversion of H₂B·NMeH₂ (δ = -17.8) relative to [H₂B·NMeH₂]₀ (δ = -5.4, br) measured by ¹¹B{¹H} NMR spectroscopy (THF solvent).

now the major species formed (~90% by ¹¹B NMR spectroscopy, Scheme 10). This process presumably occurs via metal-promoted B–N bond cleavage, possibly via a Rh σ amine–borane intermediate, to give H₂B·NMeH and H₂B·NMeH₂ which both proceed under the appropriate conditions of substrate concentration to give polyaminoborane and/or III. The formation of only III at low substrate concentration is consistent with the stoichiometric experiments using H₂B·NMeH₂ (i.e., Scheme 7). A very similar redistribution of H₂B·NMeHBH₂·NMeH₂ to afford poly(methylaminoborane) has been reported using the [Ir-(BuPOCOPBu)] catalyst, which is also suggested to operate via B–N bond cleavage and an amino–borane intermediate, although this catalyst produces polyaminoborane of higher Mₙ (67 400 g mol⁻¹, PDI = 1.4) under the conditions used. Ru(PNP)(H)(PMe₃)-based systems have also been shown, by cyclohexene trapping experiments, to promote redistribution of polyaminoborane. Addition of the secondary linear diborazane H₂B·NMe₃BH₂·NMe₃H to 1 (20 mol %) in a sealed NMR tube ultimately formed [H₂B·NMe₃]₁₁ after 24 h. After 100 min of reaction, 55% of the linear diborazane had been consumed, with H₂B·NMe₃, [H₂B·NMe₃]₁₁, and the amidodiborane (H₂B)₂(μ-H)(NMe₃)₁₁ all being observed in significant amounts. These last two species suggest B–N bond cleavage is occurring to form free NMe₃H, as has been explored computationally and kinetically in thermal rearrangements of linear diborazanes.

That both primary and secondary linear diborazanes react with complex 1 to ultimately form the final products of dehydrocoupling shows that, although they are not observed during catalysis, their formation, either transiently metal-bound or free, cannot be discounted.

2.2.2. Effect of Solvent on Polymerization. Changing the solvent to THF produced polyaminoborane (catalyst = 1, 0.2 mol %) with higher molecular weight (Mₙ = 52 200 versus 22 700 g mol⁻¹) than for C₆H₅F solvent but now taking a significantly longer time to reach near completion (19 h versus 2 h, Table 1). This suggests THF slows the rate of dehydropolymerization, possibly by the reversible formation of an adduct (cf., 4), and this may also have a role to play in attenuating any chain termination events if competitive with H₂ binding (see below). Alternatively, more of the catalyst could sit as the simple adduct species 4 leading to fewer active metal sites and thus longer polymer chains growing from the metal. THF may also solvate the growing polymer better leading to longer chain growing from the metal. Only a very small quantity of trimethylborazine, III, was observed (1–2%). THF solvent might also result in a change in mechanism to one which involves hydride donation to the metal to form a THF-stabilized borenium, that is, [(NMe₃H)(THF)BH₂]⁺.32

2.2.3. Polymer Growth Kinetics and Control over Molecular Weight Using Hydrogen. A plot of number-averaged degree of polymerization, DPₙ (DPₙ = Mₙ/M(H₂B·NMe₃H)) versus conversion for the dehydrocoupling of H₂B·NMeH₂ using 1 (0.2 mol %, open system) shows a
relationship that is suggestive of a predominately chain-growth mechanism for the growing polymer (Scheme 11). Such a similar peak profiles centered around \(\delta -5\). In particular, those at low conversions and high conversions are qualitatively the same, suggesting the nature of the polymer in each is similar.

Addition of a further 500 equiv of \(\text{H}_3\text{B}\cdot\text{NMeH}_2\) to a reaction postpolymerization resulted in further dehydropolymerization, to yield polymer with similar molecular weight and polydispersity to before \((M_n = 17 900 \text{ g mol}^{-1}, \text{ PDI} = 1.8)\), over a similar time scale. This result shows that the catalyst remains active directly after catalysis has finished but it is not a living system and there must be some chain transfer/termination process occurring.

In a closed system (Youngs flask, \(\sim 30 \text{ cm}^3\) volume, stirred), dehydropolymerization also proceeds essentially to completion (Scheme 11, Table 1) but over a much longer time scale than in an open system (24 h versus 2 h). The resulting isolated solid is waxy in appearance, suggesting a lower \(M_n\) polymer compared with the free-flowing solid produced in an open system. A \(^{11}\text{B}(^1\text{H})\) NMR spectrum of this material shows a broad, poorly resolved peak centered around \(\delta -5\) that also shows evidence for shorter-chain oligomeric species, compare \(\text{H}_3\text{B}\cdot\text{NMeHHBH}_2\cdot\text{NMeH}_2\) by an overlaid sharper signal that becomes a broad triplet in the \(^{11}\text{B}\) NMR spectrum (Figure 1b). There is also a smaller intensity signal \(\sim \delta -18\) in the region associated with \(\text{BH}_3\) groups, which is also coincident with residual \(\text{H}_3\text{B}\cdot\text{NMeH}_2\). Analysis of this material by GPC showed that the polymer produced under these conditions of exogenous hydrogen was considerably shorter than that produced in an open system \((M_n = 2800 \text{ g mol}^{-1}, \text{ PDI} = 1.8)\). This demonstrates that hydrogen potentially acts as a modifier in the catalytic process, and we suggest it acts as a chain transfer reagent, as in Ziegler–Natta ethene polymerization where hydrogen can used control polymer molecular weight.1,73

2.2.4. Probing Free \(\text{H}_2\text{B}\cdot\text{NMeH}\) as an Intermediate. As discussed in the Introduction, the hydroboration of exogenous cyclohexene has previously been shown to act as a marker for the presence of free amino–borane \(\text{H}_2\text{B}\cdot\text{NMeH}\) in dehydropolymerization reactions.22,34,37 In the presence of cyclohexene using 50 mol % of \(1\) with \(\text{H}_3\text{B}\cdot\text{NMeH}_2\), the hydroborated product \(\text{Cy}_2\text{B} = \text{NMeH}\) is observed as the major boron-containing product, alongside III as the minor product (Scheme 12). This suggests that, at low substrate concentration, free amino–borane is generated, which has sufficient lifetime for reaction with cyclohexene. By contrast, at high substrate concentrations (0.2 mol %), no hydroborated product is observed. Instead, polymer is produced, interestingly with a significantly higher molecular weight than formed in the

**Scheme 11.** (a) Degree of Polymerization versus Conversion;**b** (b) Addition of a Further 500 equiv of \(\text{H}_3\text{B}\cdot\text{NMeH}_2\) to 1 after Catalysis; (c) Control over Molecular Weight Using \(\text{H}_2\) \((\text{C}_6\text{H}_5\text{F} \text{ Solvent})\) or THF Solvent

\(^*0.2\text{ mol % }1, 0.44 \text{ M }[\text{H}_3\text{B}\cdot\text{NMeH}_2], \text{ open system. Each point is a separate experiment in }\text{C}_6\text{H}_5\text{F} \text{ with varying time, with the product precipitated with hexanes. Degree of polymerization determined by GPC. Polymer conversion measured by }^{11}\text{B}(^1\text{H})\text{ NMR spectroscopy. Data points come from three repeat analyses on the same sample, with the mean value and standard error shown.}\)**

process has been proposed previously for the \([\text{Ir}^{\text{BuPOCOP}^\text{Bu}}]_2\) catalyst system for which a modified chain-growth mechanism is invoked, in which slow dehydrogenation to form amino–borane is followed by faster metal-mediated polymerization of this unsaturated fragment.15 This suggestion is on the basis of the polymer conversion kinetics that show that high-molecular-weight polymers are present at low (less than 40%) conversion, coupled with the observation that higher catalyst loadings lead to higher-molecular-weight polymer. A similar mechanism has been proposed for the dehydropolymerization of ammonia–borane using bifunctional Ru catalysts.23 Our polymer conversion kinetics suggest a similar mechanism is operating, in that there is a high degree of polymerization at low conversion \((M_n = 30 800 \text{ g mol}^{-1}, \text{ PDI} = 1.4 \text{ at } 20\% \text{ conversion}; M_n = 25 300 \text{ g mol}^{-1}, \text{ PDI} = 1.6 \text{ at } 100\% \text{ conversion})\).22 However, in contrast to the \([\text{Ir}^{\text{BuPOCOP}^\text{Bu}}]-\text{H}_2\) systems, when the catalyst loading is increased (i.e., \(\times 5\) the loading, 1 mol %), the polymer that results is now of significantly lower molecular weight but similar polydispersity \((M_n = 7500 \text{ g mol}^{-1}, \text{ PDI} = 1.5)\). This strongly suggests a metal-centered process, as initially proposed by Baker and Dixon for the catalytic dehydrogenation of ammonia–borane.57

\(^{11}\text{B}(^1\text{H})\text{ NMR data for each conversion point show broadly similar peak profiles centered around }\delta -5\). In particular, those at low conversions and high conversions are qualitatively the same, suggesting the nature of the polymer in each is similar.

Addition of a further 500 equiv of \(\text{H}_3\text{B}\cdot\text{NMeH}_2\) to a reaction postpolymerization resulted in further dehydropolymerization, to yield polymer with similar molecular weight and polydispersity to before \((M_n = 17 900 \text{ g mol}^{-1}, \text{ PDI} = 1.8)\), over a similar time scale. This result shows that the catalyst remains active directly after catalysis has finished but it is not a living system and there must be some chain transfer/termination process occurring.

In a closed system (Youngs flask, \(\sim 30 \text{ cm}^3\) volume, stirred), dehydropolymerization also proceeds essentially to completion (Scheme 11, Table 1) but over a much longer time scale than in an open system (24 h versus 2 h). The resulting isolated solid is waxy in appearance, suggesting a lower \(M_n\) polymer compared with the free-flowing solid produced in an open system. A \(^{11}\text{B}(^1\text{H})\text{ NMR spectrum of this material shows a broad, poorly resolved peak centered around }\delta -5\) that also shows evidence for shorter-chain oligomeric species, compare \(\text{H}_3\text{B}\cdot\text{NMeHHBH}_2\cdot\text{NMeH}_2\) by an overlaid sharper signal that becomes a broad triplet in the \(^{11}\text{B}\) NMR spectrum (Figure 1b). There is also a smaller intensity signal \(\sim \delta -18\) in the region associated with \(\text{BH}_3\) groups, which is also coincident with residual \(\text{H}_3\text{B}\cdot\text{NMeH}_2\). Analysis of this material by GPC showed that the polymer produced under these conditions of exogenous hydrogen was considerably shorter than that produced in an open system \((M_n = 2800 \text{ g mol}^{-1}, \text{ PDI} = 1.8)\). This demonstrates that hydrogen potentially acts as a modifier in the catalytic process, and we suggest it acts as a chain transfer reagent, as in Ziegler–Natta ethene polymerization where hydrogen can used control polymer molecular weight.1,73

**Scheme 12.** Cyclohexene Trapping Experiments

\(^*\text{Solvent } = \text{C}_6\text{H}_5\text{F}.\)**
absence of cyclohexene ($M_w = 38\,600\,g\,mol^{-1}, \text{PDI} = 1.8$). A small amount of cyclohexane is also formed ($\sim 5\%$ conversion). This suggests that, under this concentration regime, free amino–borane is not produced in concentrations that allow for hydroboration of cyclohexene. As 2 has been reported to reduce cyclohexene to cyclohexane while becoming a Rh($I$) species, the longer polymer chain length could be a result of a lower concentration of the Rh($III$) precatalyst (e.g., 7), which would concomitantly result in fewer active sites for polymerization. Alternatively, cyclohexene could simply attenuate chain transfer by being competitive with $H_2$ for binding to the active catalyst (vide infra).

2.2.5. Kinetic Studies on $H_3B$-NMe$_2$H: Open System. The low solubilities of $H_3B$-NMe$_2$H and the resulting polyamino–borane preclude detailed solution-based kinetic investigations. We have thus conducted more detailed studies on the catalytic process occurring using soluble $H_3B$-NMe$_2$H, which ultimately dehydrogenates to give II. That both primary and secondary amine–borane systems show very similar reaction profiles (induction period, same binding mode and reactivity with the $\{\text{Rh(Xantphos)}H_2\}^+$ fragment) suggests that this approximation is a reasonable one.

Following the temporal evolution of the dehydrocoupling of $H_3B$-NMe$_2$H in an open system (i.e., under a slow flow of Ar) under different substrate concentration regimes ($0.018–0.288\,M$) while keeping the concentration of I constant ($1.44 \times 10^{-4}\,M$, i.e., 0.2 mol % at $[H_3B-\text{NMe}_2\text{H}] = 0.072\,M$) led to the concentration/time plots as exemplified in Scheme 13 (also Supporting Information and Scheme 8a). All of these plots show very similar induction periods ($\sim 400\,s$) and the formation of $H_2B=\text{NMe}_2$ as an intermediate. At higher $H_3B$-NMe$_2$H concentration, that is, 0.288 M, the rate of consumption of amine–borane after this induction period appears to be pseudo-zero-order initially, behavior that is less pronounced at lower concentrations. This might suggest that saturation kinetics are operating in this system at high $H_3B$-NMe$_2$H concentrations. To confirm this, a plot of rate of $H_3B$-NMe$_2$H consumption at constant Rh concentration versus time for each data point, excluding the induction period, over the $H_3B$-NMe$_2$H concentration range $0.018–0.228\,M$ (i.e., a 16-fold change in concentration) reveals that saturation kinetics become important at a $H_3B$-NMe$_2$H concentration of $\sim 0.1\,M$, above which a pseudo-zero-order dependence is observed (Scheme 14). At lower $H_3B$-NMe$_2$H concentration, this is now a pseudo-first-order relationship. The catalysis is first order in Rh concentration for an initial $H_3B$-NMe$_2$H concentration of 0.072 M, when the loading was varied between 0.1, 0.2, and 0.4 mol %. Kinetic isotope effect (KIE) studies measured during the zero-order phase showed a small but significant effect for exchanging N–H for N–D ($k_H/k_D = 2.1 \pm 0.2$) suggesting a primary KIE but little effect on exchanging B–H/B–D ($k_B/k_D = 0.9 \pm 0.1$). The induction period observed at the start of catalysis is approximately twice as long for NH/ND replacement and shows no change for BH/BD exchange.

These results suggest that N–H bond breaking is involved in both the turnover-limiting step during catalysis and the induction process. The KIE for NH activation is lower than that reported for $H_3B$-NMe$_2$H dehydrocoupling using Rh-($PCy_3$)$_2$($H_2$)Cl ($k_H/k_D = 5.3 \pm 1.2$) or $Cp_2Ti$ ($3.6 \pm 0.3$), as well as $H_3B$-NH$_3$ dehydrocoupling using bifunctional Ru($H(PNP)\text{H}(PMe_3)$ ($H(PNP) = \text{HN(CH}_2\text{CH}_2\text{PMe}_3)\text{H}$) ($5.3$), but is comparable to that measured for the Ni($\text{NHC})_2$ system (2.3) in which the NHC ligand is involved in N–H transfer, and Shvo’s catalyst ($1.46 \pm 0.9$), although in this last case, an H/D crossover mechanism was suggested to also operate that attenuates the observed KIE.

The postinduction period processes have been interrogated using a steady-state/saturation kinetics model that provides a good fit between observed and calculated rates (Scheme 14). In this model, the catalyst (CAT), produced via an induction process ($k_{ind}$ modeled but not further analyzed), binds $H_3B$-NMe$_2$H to form an intermediate (CAT–AB), which we propose has two amine–borane moieties (or derivatives thereof) bound. Ligation of two amine–boranes at a metal center has been observed experimentally,28 suggested from kinetic models in $Cp_2Ti$ dehydrocoupling catalysts, and explored computationally.29-30 At $H_3B$-NMe$_2$H concentrations above approximately 0.2 M, the turnover-limiting step occurs after the formation of CAT–AB, with the equilibrium between CAT and CAT–AB, if present, being strongly toward the latter.

2.2.6. Kinetic Studies on $H_3B$-NMe$_2$H: Closed System. As demonstrated by Scheme 8, performing the catalysis in a sealed NMR tube (0.2 mol % I, $[H_3B-\text{NMe}_2\text{H}] = 0.072\,M$) leads to a considerably longer time for completion of catalysis. Interest-
2.2.7. Kinetic Studies on \( \text{H}_3\text{B-NMe}_2\text{H}_2 \): Open System. In an open system, a plot of rate of \( \text{H}_2 \) evolution, excluding the induction period, at an initial \( \text{H}_3\text{B-NMe}_2\text{H}_2 \) concentration of 0.44 M and 0.2 mol % \( \text{I} \), reveals a temporal profile fully consistent with saturation kinetics, as also found for \( \text{H}_3\text{B-NMe}_2\text{H}_2 \). At concentrations of \( \text{H}_3\text{B-NMe}_2\text{H}_2 \) below 0.1 M, pseudo-first-order kinetics are observed, while above 0.1 M, there is a pseudo-zero-order dependence (Supporting Information). These observations strengthen the likely similarities in the overall mechanism between \( \text{H}_3\text{B-NMe}_2\text{H}_2 \) and \( \text{H}_3\text{B-NMe}_2\text{H} \).

2.2.8. Resting State during Catalysis: Evidence for an Amido–Borane Species? As our standard conditions of catalysis use only 0.2 mol % loadings of \( \text{I} \), the observation of resting states (i.e., \( \text{CAT} \)–\( \text{AB} \)) is difficult by NMR spectroscopy. However, by using 5 mol % \( \text{I} \) in a sealed system, the temporal evolution of the catalyst can be monitored adequately using both \( ^1\text{H} \) and \( ^{31}\text{P} \{^1\text{H} \} \) NMR spectroscopies. On addition of \( \text{H}_3\text{B-NMe}_2\text{H}_2 \) to \( \text{I} \), there is the immediate formation of \( \text{S} \) and a number of new species that we have been unable to assign definitively, although these appear to contain \( \text{Rh-H} \) moieties. Over time (3 h, 65% conversion of \( \text{H}_3\text{B-NMe}_2\text{H}_2 \)), the NMR data show that, apart from \( \text{S} \), one species is dominant. In the \( ^1\text{H} \) NMR spectrum, a broad multiplet is observed at \( \delta \sim 9.4 \), which sharpens on decoupling \( ^{11}\text{B} \) to reveal a doublet \( (J(P\text{H}) \sim 84 \text{ Hz}) \) and a broad peak on \( ^{31}\text{P} \) decoupling. These data suggest a \( \text{B-H} \rightarrow \text{Rh} \) interaction trans to a phosphine. No corresponding \( \text{Rh-H} \) signal was observed. Broad peaks observed \( \sim \delta \sim 1.15 \) are suggestive of \( \sigma \), \( \text{Rh-H} \rightarrow \text{B} \) or \( \text{Rh-H}_2 \) interactions, but as this region overlaps with that in \( \text{S} \), assignment is not definitive, and decoupling \( ^{11}\text{B} \) reveals no additional \( \text{B-H} \) signals over those for \( \text{S} \).

Inequivalent, poorly resolved phosphine environments, \( \delta \) 23 \( (J(\text{RhP}) \sim 160 \text{ Hz}) \) and \( \delta \) 4 \( (J(\text{RhP}) \sim 120 \text{ Hz}) \), are observed in the \( ^{31}\text{P} \{^1\text{H} \} \) NMR spectrum. On the basis of these data, we tentatively assign a structure to this complex as the amido–borane 8

\[
[\text{Rh}(\kappa^2\text{pp}-\text{Xantphos})(\text{H})\text{(NMe}_2\text{BH}_3)(\text{L})]\text{[BAr}_6^\text{F}_4],
\]

8 (Scheme 15). The spectroscopic data do not allow us to comment on whether \( \text{L} = \text{H}_2 \) or \( \text{H}_3\text{B-NMe}_2\text{H}_2 \). Electrospray ionization–mass spectrometry (ESI-MS) was uninformative. However, the former \( (\text{L} = \text{H}_2) \) would form under the conditions of hydrogen production in a sealed tube, and the absence of a \( \text{Rh-H} \) signal could be due to rapid hydride/dihydride exchange. 85 An alternative explanation is that 8 is a neutral Rh species that does not contain a hydride, formed by deprotonation of the \( \text{Rh-H} \) group.

These NMR data are similar to those reported for the phosphino–borane complexes such as \( [\text{Rh}(\kappa^2\text{pp}-\text{PPh}_2\text{(CH}_2)_3\text{PPh}_2)(\text{H})(\text{PPh}_2\text{BH}_3)(\text{H}_3\text{B-PPh}_2\text{H})]\text{[BAr}_6^\text{F}_4] \).
in particular, the large $^1\text{H} - ^3\text{P}$ trans coupling and chemical shift for the proposed $\beta$-agostic BH unit ($\delta = 6.9$, $J(\text{PH}) = 77$ Hz) and the chemical shifts in the $^3\text{P}^2[^1\text{H}]$ NMR spectrum for the chelating phosphine ($\delta 10.5$ J(RhP) 102 Hz; 27.2, $\delta$ J(RhP) 131 Hz). The assigned $\beta$-agostic BH group also comes at a chemical shift similar to that observed for other agostic Rh···HN interactions, for example, in the dimer $[(\text{Rh}(\text{P}^3\text{Pr})_2\text{H})_2(\sigma, \mu-H,\text{BNNMe}_3)(\mu-H,\text{B-NMe}_3)]\text{[BAR}_2^4]\_2$, ($\delta = -9.46$). A possible mode of formation of 8 from 5 could involve NH proton transfer to the hydride (protonlysis). A similar process has been suggested by computation for NH activation in H$_2$B-NH$_3$ by (Cy-PSPi)RuN(SiMe$_3$) (CyPSPi = $\kappa^3$-(Cy$_2$PC$_6$H$_4$)$_2$SiMe)$_3$.

Such a process might suggest the $N$--H activation is a cooperative process, possibly involving $N$--H--$\beta$ dihydrogen bonds.

Although we cannot fully discount an alternative formulation for 8 as base-stabilized boryl (e.g., Rh(H)BH$_2$NMe$_2$H), the temporal evolution of 8 is inconsistent with this, as $N$--H exchange is rapid (Section 2.1) compared to the induction period. Moreover, the induction period changes on NH/ND exchange, while not with BH/BD exchange, further suggesting $N$--H activation is important in the formation of the catalytically competent intermediate. Likewise, the NMR data do not allow us to discount a dimeric structure for 8. Such a motif has not been reported for [Rh(Xantphos)] complexes, and only a handful of examples with Ir, Pd, and Au are known.

The tentative, suggested structure of 8, with an amido--borane motif, has precedent with mechanistic studies on other amine--borane dehydrogenation catalyst systems: for example, group 2 catalysts, which invoke very similar intermediates for H$_2$B-NMe$_3$H (and related) dehydrogenation; Fe-based systems in which such motifs have been suggested to be key intermediates for the propagation of a polymer chain in H$_2$B-NH$_3$, dehydrocoupling; and Cp$_2$Ti$_2$ or Rh-(PCy$_3$)$_2$(H)$_2$Cl$_6$ catalysts for dehydrocoupling of H$_2$B-NMe$_3$H. Moreover, closely related phosphido--borane species have been isolated and shown to be productive intermediates in phenol borane dehydrocoupling.

### Scheme 16. Reactivity of Et$_3$B-NMe$_2$H with 2

![Scheme 16. Reactivity of Et$_3$B-NMe$_2$H with 2](image)

The $\beta$-agostic BH functionality blocked and thus acts as a potential probe for $N$--H activation only, and such an approach has recently been used in Ru(H(PNP)·(H)$_2$)(PMe$_3$)$_2$ systems to generate amido--borane species in low relative concentration. In our hands, the reaction ultimately led to the product of $N$--$N$ bond cleavage, [Rh($\kappa^3$-$\text{P}^3\text{OP}$·Xantphos)](H)$_2$(NMe$_3$H)[BAR$_2^4$]$_2$, 9 (Scheme 16), a complex that has been characterized by NMR spectroscopy and also independently synthesized by addition of NMe$_3$H to 2 (Supporting Information). No intermediate species were observed, and the fate of the borane has not been investigated.

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observed (400 s) and a similar overall time to completion compared with starting from 1 or 2, suggesting that 10b is not the active catalyst species. That the NMR data for 10a and 10b are different from that observed for the resting state in solution (i.e., 8), coupled with observation of this induction period, argues against a hydridoboryl structure for CAT or CAT–AB. The isolation and observation of B–H activated products 10c and 10b, respectively, importantly demonstrate that amino–borane fragments can interact with the \{Rh(Xantphos)\}⁺ fragment, presumably via an (unobserved) σ-amino–borane complex. Such interactions are suggested to be important in the mechanism of dehydrocoupling as discussed next.

3. DISCUSSION

Within the parameters explored by our experiments, H₃B·NMe₂H and H₃B·NMe₃H show very similar kinetic behavior in their consumption during catalysis, although the final products differ. This suggests that there is a common mechanistic framework that links the two, although certain details will be different, for example, in the final products of the B–N bond forming event. Any mechanistic scenario suggested is required to satisfy a number of criteria that flow from our observations on these two systems: (i) there is a slow induction period, which is proposed to involve N–H activation; (ii) catalysis appears to occur in the Rh(III) oxidation state, rather than a Rh(I)/Rh(III) cycle; (iii) polymer kinetics support a predominately chain-growth process, there is a single-site model for polymer propagation, and the catalyst is not living; (iv) chain transfer/termination is modified by H₂ and THF, the former resulting in shorter polymer chains, the latter in longer chains; (v) saturation kinetics operate during the productive phase of catalysis, that is, pseudo-zero-order in substrate during the early phase of productive catalysis; (vi) in a sealed system (i.e., under H₂) turnover is slower and follows a first-order decay (as measured for H₃B·NMe₃H); and this inhibition by H₂ is reversible, as opening the closed system (i.e., release of H₂) results in an increase in relative rate; (vii) at low substrate concentration, no borazine forms, and cyclohexene is hydrogenated, indicating free amino–borane; (viii) at high substrate concentration, no borazine forms, and cyclohexene is not hydrogenated; (ix) catalytic turnover proceeds via a resting state that is suggested to be an amido–borane; (x) immediately at the end of catalysis, activity is retained in both closed and open systems.

We propose the mechanism shown in Scheme 18 as one that best fits the available data. Addition of amine–borane to 1 results in rapid dehydrogenation and hydrogen transfer to the metal, presumably via a transient sigma complex A, to give a Rh(III) dihydride (e.g., 5). This can also be accessed by direct addition of amine–borane to the preformed Rh(III) complex 2. Subsequent slow N–H activation results in the formation of the proposed amido–borane CAT that can rapidly but reversibly combine with additional amine–borane to form CAT–AB. CAT–AB then undergoes further NH/BH transfers involving turnover limiting N–H activation. For H₃B·NMe₃H, this results in the production of amino–borane H₂B·NMe₂ that subsequently dimerizes to give II. For H₃B·NMe₄H, there is an accompanying B–N bond-forming event that results in a propagating polymer chain on the metal center. We cannot completely discount a similar process occurring for H₃B·NMe₂H, as shown for Cp₂Ti\[Rh(PR₃)₂\]⁺,¹⁸,²¹ and group 2 catalysts,⁸¹ which give H₃B·NMe₂BH₂·NMe₄H. However, if this is occurring, B–N bond cleavage must be kinetically competitive as, unlike these other systems, we see no significant amounts of H₂B·NMe₂BH₂·NMe₄H, either free or metal bound. There are systems in which this diborazine has been suggested not to be involved as an intermediate,¹⁸,²¹ which also dehydroamoridize H₂B·NMe₄H.

Although we can only speculate as to the likely intermediates/transition states during these turnover-limiting processes, especially as complex 8 is not fully characterized, a key requirement for H₃B·NMe₄H dehydroamoridization is that any suggested pathway results in overall insertion of an amino–borane unit, as this provides a template for a growing polymer chain at a metal single site, that is, a chain-growth mechanism. In addition, at high H₃B·NMe₄H concentration, free amino–borane is not produced in a kinetically significant amount based upon cyclohexene trapping experiments. We suggest one possible mechanism for the B–N bond-forming event as shown in Scheme 19, in which relatively slower dehydrogenation of H₃B·NMe₄H (with N–H activation being rate limiting) affords a weakly bound “real monomer” amino–borane¹⁰¹ that then undergoes rapid B–N bond formation. A key component of this mechanism is that the Rh–amido–borane motif is retained throughout and that the B–N bond forming process results in formal insertion of the amino–borane into the Rh–N bond. We are unable to comment on the precise coordination motif of the Xantphos ligand during.

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Figure 2. Solid-state structure of the cation in 10c showing displacement ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): Rh1–B1, 2.034(3); Rh1–P1, 2.2681(7); Rh1–P2, 2.268(4)(7); Rh1–O1, 2.2842(17); Rh1–N2, 2.135(2); B1–N1, 1.378(4); B1–Rh1–O1, 175.53(11); B1–Rh1–P1, 96.53(10); B1–Rh1–P2, 100.17(10); N1–B1–Rh1, 133.9(2).
these steps, as $κ^2$-P,P and $κ^3$-P,O,P coordination modes are both accessible.\textsuperscript{53,54}

Dihydrogen acts as a chain-transfer agent. At lower H$_3$B·NMe$_2$ concentration or high H$_2$ concentration under sealed tube conditions, binding of H$_2$ could well become competitive with amine–borane coordination in CAT–polymer. Chain termination by heterolytic cleavage\textsuperscript{102} of the coordinated H$_2$ could return a Rh(III)H$_2$ fragment (i.e., 5) and the free polymer. We suggest that THF also acts to modify the catalyst by binding competitively with both H$_2$ and amine–borane (i.e., CAT−L, Scheme 18). This slows down productive catalysis but also attenuates chain transfer, so that longer polymer chains result. Under stoichiometric conditions of low concentration of H$_3$B·NMe$_2$, borazine III is formed. This could either occur from 5 by successive slow BH/NH transfer steps or from CAT that under such conditions would find no stabilization from additional amine–borane and could undergo B−H β-hydrogen transfer to form H$_2$B$\equiv$NMe$_2$ (that then trimerizes/loses H$_2$) and a RhH$_2$ species. Consistent with the formation of amino–borane at low H$_3$B·NMe$_2$ concentration, cyclohexene is hydroborated under these conditions.

This general mechanistic scheme can also be used to speculate upon the dehydrogenation pathway of the secondary amine–borane H$_3$B·NMe$_2$. Formation of CAT–AB and BH/NH transfer leads to an amino–borane intermediate (Scheme 20) but now with H$_3$B·NMe$_2$ bound. This can simply either lose the bulkier H$_2$B$\equiv$NMe$_2$ fragment that then dimerizes to form II (pathway a) or undergo an H-transfer process\textsuperscript{103} from BH$_2$ to BH$_2$ to generate an alternate amido–borane and free H$_2$B$\equiv$NMe$_2$ (pathway c). With the current data in hand, we cannot discriminate between these two processes. We suggest that B−N coupling in the secondary amine–borane is disfavored due to steric grounds (pathway b), as we have

\textsuperscript{“[Rh] = [Rh(Xantphos)](H)”.

Scheme 18. Suggested Mechanistic Cycle and Intermediates for the Dehydrocoupling of H$_3$B·NMe$_2$H and the Dehydropolymerization of H$_3$B·NMeH$_2$\textsuperscript{a}

\textsuperscript{a}$^{“}$For H$_3$B·NMe$_2$, R′ = H or growing polymer chain, R = H. For H$_3$B·NMe$_2$H, R = Me, R′ = H.

Scheme 19. Postulated Pathway, Based upon the Suggested Intermediates, for the B−N Coupling Event in H$_3$B·NMeH$_2$ Dehydropolymerization\textsuperscript{a}

\textsuperscript{a}$^{“}$[Rh] = [Rh(Xantphos)](H).
recently explored in the formation (or lack of) oligomeric amino–boranes on [Ir(PCy3)(H)]+ fragments with H3B-NH3 (oligomers), H3B-NMeH2 (linear dimer), and H3B-NMe2H (amino–borane), in which sterics play an important role.104

4. CONCLUSIONS

A detailed mechanistic study on the dehydrocoupling of H3B-NMe2H and dehydropolymerization of H3B-NMeH2, using the [Rh(Xantphos)]+ fragment suggests that similar mechanisms operate for both, which only differ in that B–N bond formation (and the resulting propagation of a polymer chain) is favored for H3B-NMeH2, but not H3B-NMe2H. The key feature of this suggested mechanism is the generation of an active catalyst, proposed to be an amido–borane, that then reversibly binds additional amine–borane so that saturation kinetics operate during catalysis. B–N bond formation (with H3B-NMeH2) or elimination of amino–borane (with H3B-NMe2H) follows. Importantly, for the dehydropolymerization of H3B-NMeH2, we also demonstrate that polymer formation follows chain-growth processes from the metal and that control of polymer molecular weight can also be achieved by using H2 or THF solvent. Hydrogen is suggested to act as a chain-transfer agent, leading to low-molecular-weight polymer, while THF acts to attenuate chain transfer, and accordingly, longer polymer chains are formed. Although the molecular weights of polymeric material obtained are still rather modest compared to the previously reported [Rh(−BuPOCOPBu)(H)]+ system, the insight available from using the valence isoelectronic [Rh(Xantphos)-(H)]+ fragment leads to a mechanistic framework that explains the experimental observations and polymer growth kinetics. The suggested mechanism for dehydropolymerization is one in which the amido–borane species dehydrogenates an additional H3B-NMeH2 to form the “real monomer” H3B-NMeH that then undergoes insertion into the Rh–amido bond to propagate the growing polymer chain on the metal. This is directly analogous to the chain-growth mechanism for single-site olefin polymerization.† A future challenge is thus to use this insight to develop catalysts capable of living polymerization and/or control of polymer tacticity as so elegantly demonstrated with polyolefin chemistry; it will be interesting to see whether the mechanistic themes discussed here are applicable in a more general sense to other catalyst systems.

ASSOCIATED CONTENT

Supporting Information
Experimental and characterization details, including NMR data, X-ray crystallographic data, polymer characterization data and kinetic plots. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center (CCDC) and can be obtained via www.ccdc.cam.ac.uk/data_request/cif.

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Notes
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