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Amine-Borane Dehydropolymerization using Rh-based Pre-Catalysts: Resting State, Chain-Control and Efficient Polymer Synthesis.

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A detailed study of H₂B·NMe₂ dehydropolymerization using the cationic pre-catalyst [Rh(DPEphos)(H₂BNMe₂CH₂CH₂Bu)]-[BAR₅]₂ identifies the resting state as dimeric [Rh(DPEphos)H₂]₂ and boronium [H₂B(NMe₂)]⁺ as the chain-control agent. [Rh(DPEphos)H₂]₂ is conveniently generated in situ from Rh(DPEphos)(benzyl), and catalyzes polyaminoborane formation, M₆ = 15000 g mol⁻¹. Closely-related Rh(Xantphos)(benzyl) operates on gram scale, at 0.1 mol%, to afford higher molecular weight polymer [M₆ = 85000 g mol⁻¹] with low residual [Rh], 81 ppm. This insight offers a mechanistic template for dehydropolymerization.

The catalyzed dehydropolymerization of amine-boranes, archetypically H₂B·NMe₂, is an atom-efficient methodology for the synthesis of polyaminoboranes (H₂BNR₂), (Scheme 1A), forming H₂ as the only by-product. This new class of main-group polymer is based upon BN main-chain units, and is isosteric with technologically-mature polyolefins. These main-chain B–N units suggest, in addition to unexplored material and chemical properties, potential applications as piezoelectric materials, or as precursors to boron-based ceramics and h-BN. The currently accepted overarching mechanism for polymer formation from amine-borane involves initial dehydrogenation to form a transient aminoborane (H₂B=NHR₂), that then undergoes end-chain nucleophilic B–N bond formation, initiated by the catalyst. While non-catalytic routes have been reported, in terms of overall efficiency, scalability, substrate scope, and control of the polymer characteristics, catalytic routes offer the broadest opportunity for the tailored synthesis of polyaminoboranes.

Scheme 1. (A) Amine-Borane Dehydropolymerization, (B) Exemplar Pre-Catalyst Systems.

A wide range of pre-catalyst systems have been described for amine-borane dehydropolymerization (Scheme 1B). After the original report of high molecular weight polymer formed using Ir(POCOP)H₂ A [POCOP = κ²-1,3-(Bu₂PO)₃C₆H₃], systems based on group-4 metalloccenes B, cooperative ligands C, and cationic [RhL₂]⁺ pre-catalysts (L₂ = e.g., Ph₃P(CH₂)₂PPh₂, DPEphos, Xantphos) D, have been described. For the Rh-based catalysts we have reported speculation, kinetics and degree of polymerization studies. These are broadly generalized by: an induction period, a non-living chain-growth propagation, an inverse relationship between catalyst loading and degree of polymerization, and H₂ acting as a chain controlling agent to reduce polymer chain length, and the catalytic cycle.

Scheme 2: Exemplar Complex 1 and Prior Observations.

| General Observations |
|----------------------|
| Chain-growth mechanism |
| Induction period |
| H₂ lowers M₆ |
| Increasing [cat] lowers M₆ |

Add NMe₂

Removes induction period
Increases M₆
[cat]²⁺
[Ir(POCOP)H₂] = 41 during catalysis

Active catalyst, chain–control agents, targeted synthesis of new catalysts, control of dehydropolymerization
H₂, on the degree of polymerization. Despite these advances, the precise details of initiation, propagation and termination remain to be determined for these diverse catalyst systems, while identification of resting states is rare and challenging. Herein we report on an investigation of the [Rh(DPEphos)]²⁺ pre-catalyst system, 1, in which a study of the kinetics, speciation and synthesis has allowed identification of the active catalyst, as well as the polymer-growth/termination processes to be interrogated. These insights are then harnessed in the design of a new, efficient, Rh-based catalyst that produces polyaminoborane on scale. A simple protocol is also described to significantly reduce the levels of residual catalyst in the isolated polymer.

We have previously reported that when 1 is employed as pre-catalyst, the monocationic hyridro-aminoborane dimer [Rh₂(DPEphos)₂(μ-H)(μ-H₂B=NMMe)] [BAR₄] 2 is formed during the early stages of reaction. We propose this arises via an amine-promoted B–H hydride transfer in a precursor catonic σ-amine borane complex [Rh(DPEphos)(H₂B-NMeH)] [BAR₄], 27 to generate a neutral hydride of empirical formula Rh(DPEphos)H (Scheme 3). Similar hydride species are formed in [Rh(PO(OPh)(H₂B-NMeH)]²⁺ 25 and [Rh(PR₃)(CH₃)₂P(CO)₃(H₂B-NH₃)]²⁻ 26 systems, alongside H₂B=NMe₂/[NH₂Me₂]²⁻ or boronium [H₂B(NH₂Me₂)]³⁻ respectively. Based on these observations, a simple kinetics model was constructed for the induction process, involving generation of 2 by rapid trapping of Rh(DPEphos)H with unreacted E, followed by a slow, amine-dependent, fragmentation to form the active catalyst. This tele-scopes the elementary steps of the induction process, 29 allows H₂ evolution to be used as proxy for transient H₂B=NMMeH, and successfully reproduces the temporal concentration profiles, 23 as a function of [Rh]TOTAL (0.2 and 0.4 mol%) or when NMeH₂ is added; Scheme 3. A VNTA analysis 30 supports the observation of an empirical fractional order in pre-catalyst: [Rh]TOTAL 0.5.

Scheme 3. Model and Fitted data. [BAR₄]²⁻, DPEphos Not Shown. [H₂B-NMeH₂] = 0.223 M (1,2-FC₆H₄).

Addition of excess H₂B-NMeH₂ to the amine complex [Rh(DPEphos)(NMeH₂)]³⁻ [BAR₄], 5, 23 also generates 3, together with boronium [H₂B(NMeH₂)]²⁻ ([18B] ~ 7.8). Solutions of complex 3 in 1,2-FC₆H₄ or in THF, irreversibly lose H₂ on degassing, to form an insoluble yellow/brown powder, analyzing as [Rh(DPEphos)H]₆, likely to be a coordination polymer with Rh–H–Rh linkages. While the Rh-polymer does not dissolve on addition of H₂, the soluble complex 2 is regenerated when [H₂B(NMeH₂)(OEt)] [BAR₄] is added. 31 Thus, when using a cationic pre-catalyst (i.e. 1 or 5), persistent NMeH₂ will favor soluble neutral hydride via equilibration with complex 2 (k₅, Scheme 3). When using neutral pre-catalyst 4, a high initial concentration of amine-borane, e.g. [H₂B-NMeH₂]₀ = 0.446 M in THF, inhibits the formation of a precipitate. Presumably, the amine-borane intercepts Rh(DPEphos)H before it oligomerizes. Thus, dimeric, neutral, hydride 3 is observed as the common resting state, irrespective of the pre-catalyst, or solvent. The half order dependence in [Rh]TOTAL points to a rapid endergonic equilibrium between dimer and monomer, prior to the turn-over limiting step. This has been noted in other Rh₃H₄ systems, 32,36,37 and the data are thus consistent with the resting state being dimeric. An important difference between neutral versus cationic pre-catalysts, is that the latter generate a boronium coproduct, which has important implications for the dehydropolymerization, as discussed next.

Neutral pre-catalyst 4 was deployed in the dehydropolymerization of H₂B-NMeH₂ at a variety of catalyst loadings, Table 1. In 1,2-FC₆H₄ as solvent, kinetics measurements were hampered by formation of the insoluble precipitate. In THF, the endometric measurements on H₂ production were less reliable due to solvent volatility. Nevertheless, polymerization goes to completion in both solvents, selectively forming [H₂BNMeH₂]₄, Figure 1A. 38 A plot of conversion versus Mₖ (Figure 1B, relative to polystyrene standards) 31,16 is characteristic of a non-living chain-growth polymerization: at low conversions the polymer is formed with high Mₖ and H₂B-NMeH₂ dominates. Variations in catalyst loading did not affect the degree of polymerization of the resulting polyaminoborane, in either 1,2-FC₆H₄ (Figure 1C, Mₖ = 15000 g mol⁻¹) or THF solutions (Mₖ = 17000 g mol⁻¹), under ‘open conditions’ with a slow Ar-flow. This is different to cationic pre-catalysts with Mₖ scales inversely with [Rh]TOTAL: e.g. 6400 (1 mol%), 34900 g mol⁻¹ (0.2 mol%), 23 However, ‘closed conditions’ that allow for build-up of H₂ result in very low molecular weight oligomers being
The reactive monomer, \( H_2B=\text{NMeH}_2 \), isobaric conditions under flow of Ar, end point determined by \(^{11}B\) NMR spectroscopy. Relative to polystyrene standards; triple column; RI detection; THF with 0.1 w/w \% [NBu][Br]; 35 °C; [sample] = 2 mg cm\(^{-3}\). THF solvent. \( M_m \) of the polymer distribution obscured by [BAR\(^+\)] signal. \( 5 \) M, 1.1 g scale.

formed (1 mol % 4, less than 1000 g mol\(^{-1}\) by GPC, \(^{11}B\) NMR spectroscopy\(^{21}\)); The cationic pre-catalyst 1 behaves analogously.\(^{22}\)

The neutral and cationic pre-catalyst systems differ by the presence of a boron co-product with the latter, the relative concentration of which will scale with [Rh]\(_{\text{TOTAL}}\).\(^{39}\) Given the underlying insensitivity to the degree of polymerization to [Rh]\(_{\text{TOTAL}}\) when using neutral 4, we thus considered whether with cationic pre-catalysts boronium \([H_2B(\text{NMeH})_2][\text{BAR}^+]\) can act as a chain-control agent to modify \( M_m \). To test this, \([H_2B(\text{NMeH})_2][\text{BAR}^+]\) was doped (0.25 to 1 mol%) into 1 mol% 4 / \( H_2B=\text{NMeH}_2 \), to selectively form polyaminoborane \((^{11}B\) NMR). Although GPC analysis of the resulting polymer using refractive index detection is affected by the co-eluting [BAR\(^+\)] masking the lower molecular weight region (Figure 1D),\(^{13}\) there is a qualitative trend of decreasing \( M_m \) with increasing \([H_2B(\text{NMeH})_2][\text{BAR}^+]\), Table 1. This outcome is consistent with boronium acting as a chain-control agent. Chain Length Distribution (In–CLD) analysis of high molecular weight fractions in GPC has been shown to be useful where there is overlap between distributions of polymer and transfer agents, such as that noted here, allowing for chain control processes to be probed.\(^{20}\) A Mayo-type plot of [boronium]/[H\(_2\)B–NMeH\(_2\)] versus the In–CLD slope indicates an inversely linear relationship (Figure 1E and F), further supporting the conclusion that the boronium functions as a rapid chain control agent in the dehydropolymerization.

Collectively, the analysis above facilitates the construction of a mechanistic landscape for dehydropolymerization, Scheme 5, that is consistent not only with the results herein, but also with our previous observations on cationic Rh-based systems.\(^{5,22,23,28,41}\) Thus, dehydrogenation of amine-borane to give the reactive monomer, \( H_2B=\text{NMeH} \), occurs at a neutral [Rh–H] species, in an H\(_2\)-mediated equilibrium with dimer 3.

Dehydrogenation to form \( H_2B=\text{NMeH} \), via BH/NH activation (Scheme 5A) could be facilitated by a hemilabile DPEphos ligand (e.g. κ\(^2\) and κ\(^3\) coordination\(^{43}\) as previously suggested.\(^{43}\)

### Table 1 GPC Characterization Data\(^{4}\)

| Entry | Cat. | [Rh]\(_{\text{TOTAL}}\) (mol%) | \( M_m \) (g mol\(^{-1}\))^\(a\) | D | [boronium] (mol%) |
|-------|------|-------------------------------|-----------------------------|---|------------------|
| 1     | 4    | 0.25                          | 15000                       | 2.5 | 0                |
| 2     | 4    | 0.5                           | 15000                       | 2.5 | 0                |
| 3     | 4    | 1                             | 15000                       | 2.4 | 0                |
| 4     | 4\(^c\) | 0.5                          | 17000                       | 2.3 | 0                |
| 5     | 4\(^c\) | 1                            | 17000                       | 2.4 | 0                |
| 6     | 4    | 1                             | [25000]                     | n/a | 0.25             |
| 7     | 4    | 1                             | [21000]                     | n/a | 0.5              |
| 8     | 4    | 1                             | [<19000]\(^d\)             | n/a | 1                |
| 9     | 6    | 1                             | 88000                       | 1.5 | 0                |
| 10    | 1    | 1                             | 21000                       | 1.5 | 1                |
| 11    | 6\(^c\), 2\(^e\) | 0.1                           | 85000                       | 1.5 | 0                |
| 13    | 7    | 1                             | 98000                       | 1.6 | 0                |

\(^a\) 298 K, 1.2–F\(_2\)C\(_6\)H\(_4\), 0.223 M \( H_2B=\text{NMeH}_2 \), isobaric conditions under flow of Ar, end point determined by \(^{11}B\) NMR spectroscopy.

\(^b\) Relative to polystyrene standards; triple column; RI detection; THF with 0.1 w/w \% [NBu][Br]; 35 °C; [sample] = 2 mg cm\(^{-3}\).

\(^c\) THF solvent. \( M_m \) of the polymer distribution obscured by [BAR\(^+\)] signal. \( 5 \) M, 1.1 g scale.

### Figure 1. Polyaminoborane data obtained using catalyst 4 (Ar flow, 1.2–F\(_2\)C\(_6\)H\(_4\), \( H_2B=\text{NMeH}_2 = 0.223 \) M) (A) \(^{11}B\) NMR spectrum of polymer; (B) \( M_m \) versus conversion; (C) GPC data for 1.0, 0.5 and 0.25 mol% catalyst loadings; (D) GPC data for 1.0 mol% 4 with \([H_2B(\text{NMeH})_2][\text{BAR}^+]\) doping. (E) In–CLD plot of high \( M_m \) fraction (D). (F) Mayo analysis.

### Scheme 5. Proposed (A) Catalyst Evolution/Dehydrogenation, (B) Propagation, (C) Chain–Control Events.
Initiated by a formal hydride-transfer from the rhodium hydride, that is now playing a dual role in both dehydrogenation and initiation, H₂B–NMeH then undergoes rapid head-to-tail end-chain nucleophilic B–N bond formation, as proposed previously (Scheme 5B). Chain-control by protonation of the terminus nucleophilic amine of the polyamide group by boron returns a cationic pre-catalyst, aminoborane and NMe₂, that are rapidly recycled (Scheme 5C). A related intramolecular proton transfer has been proposed by Paul and co-workers for In(POCOP)H₂ systems. We speculate that, in the absence of boronium, chain transfer to pre-monomer H₂B-NMe₂ controls chain-length, Scheme 5C. Whatever the precise mechanism for these chain-control processes, they result in relatively narrow dispersities of the final isolated polymer, and constant degrees of polymerization during propagation (Figure 1B). H₂ loss from 3, and related systems, occurs readily on degassing. The position of the initial monomer/dimer equilibrium is thus expected to be sensitive to [H₂], impacting on the rate of dehydrogenation as well as initiator concentration. This, we suggest, is the origin of the low degrees of polymerization observed under 'closed conditions'. In support of this, for a system where hydride-bridged dimer formation is disfavoured due to sterics, Rh(Xantphos-Pr)H₂, H₂ does not act to modify the degree of polymerization. The precise gearing of all of these interconnected relationships is therefore pre-catalyst, co-product (e.g. boronium) and solvent specific.

The use of new pre-catalysts based upon neutral 4 demonstrates wider applicability (Figure 2, Table 1). For example, the Xantphos benzyl complex, 6, is an effective precatalyst for dehydropolymerization (1 mol%, 88000 g mol⁻¹, D 1.6), and the degree of polymerization can be controlled by [H₂B(NMe₂)₂][BAR₄], e.g. 1 mol% Mₑ = 21000 g mol⁻¹. Complex 6 can be used at low loadings and high [H₂B-NMe₂] (0.1 mol%, 5 M in THF, using commercially sourced amine-borane), to produce high molecular weight polyaminoborane on gram scale (85000 g mol⁻¹, 1.1 g). Use of activated charcoal in the polymer work-up reduces the [Rh]-content from 195 ppm (no workup) to 81 ppm. This is considerably lower than reported for other Rh and Co dehydropolymerization systems. The simple benzyl-dppp-catalyst 7 also promotes formation of high molecular weight polyaminoborane (98000 g mol⁻¹).

In summary, the identification of the catalyst resting state, the events that lead to its formation, and thus the role that co-products such as boronium and H₂ likely play in chain-control, have provided important insights into the complex and nuanced set of interconnected processes that are required for selective amine-borane dehydropolymerization using Rh(bisphosphine)-based catalysts. While the detailed elucidation of the elementary steps awaits further study, Scheme 5 provides a testable framework for the analysis and design of catalyst systems for controlled amine-borane dehydropolymerization.

ASSOCIATED CONTENT

Supporting Information

Full experimental, structural, kinetics data and details of the simulated model. The Supporting Information is available free of charge on the ACS Publications website.

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Author Contributions

The manuscript was written through contributions of all authors.

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Evolution of a Dehydropolymerization Catalyst

\[ H_2B(NMeH_2)_2 \rightarrow H_2 \cdot N_{\text{ring}} \cdot N_{\text{ring}} \cdot \text{MeH} \]