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The Simplest Amino-borane H₂B–NH₂ Trapped on a Rhodium Dimer: Pre-Catalysts for Amine-Borane Dehydropolymerization

Amit Kumar, Nicholas A. Beattie, Sebastian D. Pike, Stuart A. Macgregor,* and Andrew S. Weller*

Abstract: The μ-amino–borane complexes [Rh₂(L₅)₂(μ-H)(μ-H₂B=NRH)][BAR₄]₄ (L₅=R₉P(CH₃)₃PR₉; R=Ph, Pr; R’=H, Me) form by addition of H₂B-NMe₂R'H₂ to [Rh(L₅)₂(μ-C₇H₇F)][BAR₄]. DFT calculations demonstrate that the amino–borane interacts with the Rh centers through strong Rh-H and Rh-B interactions. Mechanistic investigations show that these dimers can form by a boronium-mediated route, and are pre-catalysts for amine-borane dehydropolymerization, suggesting a possible role for bimetallic motifs in catalysts.

Polyamino-boranes [(H₂BNRH)₄] are potentially exciting new materials that are isoelectronic with technologically pervasive polyolefins, but are chemically distinct because of (H−)JB−NH(−) polarization. They are formed by the dehydropolymerization of amine-boranes (H₂BNRH₂; R=H or Me, for example; Scheme 1A), and metal-catalyzed routes to polyamino-boranes offer the potential for fine control over molecular weight and polymer stereochemistry.

[ harassment removed for clarity ]

Scheme 1. A) Amine-borane dehydropolymerization; B) a suggested coordination/insertion mechanism, P= polymer chain; C) examples of H₂B−NH₂ coordinated to a metal center.

There is recent evidence that these processes occur at a metal center in which the catalyst needs to perform two roles: 1) formal dehydrogenation of amine-borane to form a latent source of amino-borane (H₂B=NRH), and 2) subsequent B–N bond formation.[3,4] For some systems a coordination/insertion mechanism is proposed, although the precise structure of the propagating species is currently unresolved (Scheme 1B).[3,4] This is in contrast to olefin polymerization, in which the feedstock (for example, ethene or propene) is already unsaturated, and the active species and propagating mechanisms are well-defined.[7] A clearer understanding of how the catalyst dehydrogenates amine-borane, traps intermediate amino-boranes, and promotes B–N bond-formation, is central to harnessing the full potential of systems that ultimately deliver new well-defined B–N polymeric materials on a useful scale.

Unlike ethene (H₂C=CH₂), which is stable under ambient conditions, the isoelectronic amino-borane (H₂B=NH₂) has only been prepared in low temperature matrices and oligomerizes above −150°C.[2,8] Adding steric bulk to the nitrogen atom increases stability, so that, for example, H₂B=NMec₂[9] or H₂B=NBuH[10] can be observed as transient species using in situ NMR spectroscopy before they also oligomerize. There are two examples where unstable H₂B=NH₂ can be trapped by coordination to a single metal center. These originate after dehydrogenation of a putative o-ammonia borane[11] complex, forming Ru(PC₃)(H)(η²-H₂B=NH₂) A[12] and (Cy-PSiP)-Ru(H)(η²-H₂B=NH₂) B. Cy-PSiP = k₂(Cy₂PC₆H₄)SiMe.[13]

We now report that H₂B−NH₂ can be trapped by a bimetallic [Rh₂(R₉P(CH₃)₃CH₂PR₉)₂]⁺ fragment to give a novel bridging amino-borane bonding motif. We provide mechanistic evidence for formation of the complex from a monometallic precursor, and show that such dimeric amino-borane species may be important in dehydropolymerization pathways. This report builds upon previous observations that indirectly implicate bimetallic motifs during catalysis.[14–16]

Addition of a slight excess of H₃B·NH₃ to a [D₂]THF solution of [Rh₂(L₅)₂(μ-H)(μ-H₂B=NRH)][BAR₄] I (L₅=R₉P(CH₃)₃PPh₃; Ar=3,5-(CF₃)₂C₆H₄) resulted in the rapid formation of a bimetallic monocation, which was identified by NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS), and single-crystal X-ray diffraction, as [Rh₂(L₅)₂(μ-H)(μ-H₂B=NH₂)][BAR₄] 3. One equivalent of the boronium[15,16] cation [THF-BH₂-NH₂][BAR₄] was also formed (δ(B)¹H) 0.5 (t). J₁₁=108 Hz; lit.[19] [Et₂O-BH₂-NH₂][BAR₄] δ(B)¹H 0.2, J₁₁=125 Hz).

In situ solution NMR data for 3 show a signal at δ(B)¹H 51.5, a single ¹P environment (δ(¹P) 18.2, J₁₁=142 Hz), and a broad peak at δ(H)−7.45 (integral ca. 3H relative to the
phenyl groups). ESI-MS shows a mono-cation at m/z = 1060.16 (calcld 1060.16) with the correct isotope pattern. Crystallization (THF/pentane/18°C) gave a small number of crystals, for which a single-crystal X-ray diffraction study showed a H₂B–NH₂ unit bridging a [(Rh₂(L₄)₆(μ-H)) unit (Supporting Information, Figure S21). However, insufficient material was obtained on which to collect reliable NMR data. Complex 3 is unstable in solution at room temperature, decomposing after four hours to give a mixture in which [Rh(L⁴)](THF)₃][BArF₄] was present in approximately 30% yield.[21] To put the structure and spectroscopic data on a firm footing, the equivalent reaction using the Pr-substituted chelating phosphine gave complex 4, [Rh₂(L₄)₆(μ-H)(μ-H₂B=NH₂)][BArF₄], and 5 (Scheme 2).

This reaction was slower than that observed for L⁴. Complex 4 can also be isolated in 78% yield as orange crystalline material using an alternative route (see below, Scheme 5). In the absence of H₂B–NH₂, complex 4 is stable for at least two days in D₂O/THF solution. However, when formed in situ 4 decomposes over 24 hrs into a mixture of products, one of which can be characterized as [Rh₂(L₄)](H₂O)(μ-H₂B=NH₂)][BArF₄],[22] The room temperature solution NMR data obtained for 4 are very similar to those for 3: δ(B) 51.1; δ(P) 40.8. J₈₂ = 142 Hz; δ(H) = −8.64 (3H, broad). Progressive cooling to 180 K splits the high field hydride resonance into two signals, in a 2:1 ratio; while two ³¹P environments were also observed, suggesting a fluxional process at room temperature. An Eyring plot yields the activation data: ΔH° = 31.1 ± 1.3 kJ mol⁻¹, ΔS° = 0.27 ± 1.7 K⁻¹ mol⁻¹. ΔG(298 K) = 39.2 ± 1.6 kJ mol⁻¹; where the negative entropy of activation suggests an intramolecular process (Supporting Information, Figures S2–3).

The solid-state structure of complex 4 is shown in Figure 1A. A dimeric Rh unit is accompanied by one [BArF₄]⁻ anion, confirming that it is a mono-cation. Two [Rh(L⁴)]⁺ fragments are bridged by a hydride and a H₂B–NH₂ unit. The B–N distance (1.377(6) Å) is consistent with a significant B–N π-interaction, and is similar to that measured in A (1.396(3) Å) and B (1.359(8) Å), as well as the bridging borylene complex C (1.399(3) Å, Scheme 3).[23] The Rh–B distances (2.070(5) and 2.055(5) Å) are similar to those found in the amino-borane complexes A, B, and [Ir(PC₅)₂(H₂B=NH₂)][BArF₄],[24] (spanning 1.956(2) to 2.140(13) Å), but significantly shorter than those measured in the bridging thexylborohydride complex D (2.330(3) Å).[25] The hydrogen atoms were located but refined using a riding model. Within the limits of X-ray diffraction the B–H distances suggest lengthened, but unbroken bonds (for example, 1.360 Å). The NH₂ group is slightly twisted with respect to the BH₂ group (24.3°; Figure 1B). The whole H₂B–NH₂ fragment lies 54.1° from the Rh–Rh vector so as to accommodate appropriate overlap between the B–H bonds and the two rhodium centers. These are best described as being two distorted square planes (for example, P1/P2/H3/H1) twisted with respect to one another by 102° (Figure 1C). This motif, which is similar to that observed for D, is fully consistent with the low temperature NMR data, and are recreated well in the DFT calculated structure (Supporting Information, Figures S24–26). Each metal center in 4 is best described as RhI, with no M–M bond.[26] The end-on [Rh₂(μ-H₂B=NH₂)] binding mode contrasts with H₂C=CH₂ that bridges two metal centers symmetrically using both

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1. Crystallization (THF/pentane/18°C) gave a small number of crystals, for which a single-crystal X-ray diffraction study showed a H₂B–NH₂ unit bridging a [(Rh₂(L₄)₆(μ-H)) unit (Supporting Information, Figure S21).
2. In the absence of H₂B–NH₂, complex 4 is stable for at least two days in D₂O/THF solution.
3. Progressive cooling to 180 K splits the high field hydride resonance into two signals, in a 2:1 ratio; while two ³¹P environments were also observed, suggesting a fluxional process at room temperature.
4. The solid-state structure of complex 4 is shown in Figure 1A. A dimeric Rh unit is accompanied by one [BArF₄]⁻ anion, confirming that it is a mono-cation.
5. Two [Rh(L⁴)]⁺ fragments are bridged by a hydride and a H₂B–NH₂ unit. The B–N distance (1.377(6) Å) is consistent with a significant B–N π-interaction, and is similar to that measured in A (1.396(3) Å) and B (1.359(8) Å), as well as the bridging borylene complex C (1.399(3) Å, Scheme 3).
6. The Rh–B distances (2.070(5) and 2.055(5) Å) are similar to those found in the amino-borane complexes A, B, and [Ir(PC₅)₂(H₂B=NH₂)][BArF₄], (spanning 1.956(2) to 2.140(13) Å), but significantly shorter than those measured in the bridging thexylborohydride complex D (2.330(3) Å).

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**Scheme 2.** Formation of amino-borane coordinated dimers 3 and 4. [BArF₄]⁻ anions are not shown.
carbon atoms, in either $\mu$-$\eta^*:\eta^*$ or $\mu$-$\eta^*:\eta^*$ bonding modes,\cite{27,28} highlighting the differences between these isosteres.\cite{29}

Surprisingly, the amino-borane in 4 is quite strongly bound. It is only slowly displaced by excess acetonitrile (7\% in 50 min) to give a mixture of species, one of which is [Rh(L\(5^p\))(N(Me)\(_2\))\(_3\)][BARF\(_2\)].\cite{22} No reaction occurs with toluene, which might be expected to form a [Rh(L\(5^p\))(\eta\(^2\)-C\(_6\)H\(_5\))\(_2\)] complex if a mononeric [Rh(L\(5^p\))] fragment were accessible.\cite{30} Addition of cyclohexene, shown to be a probe for free H\(_2\)BH\(_2\),\cite{31} gave no reaction. In contrast, H\(_3\) rapidly reacts with 4 to form [Rh(L\(5^p\))(H)\(_2\)(\mu-H)\(_3\)][BARF\(_2\)].\cite{12,32}

There are two limiting forms for the structure of 4 (and quasi-isostuctural 3): 1) a bridging amino-borane at two Rh\(_1\) centers, or 2) a bridging borylene dihydride (Rh\(_{III}\)), Scheme 3. The observed $\delta^{(11B)}$ chemical shift of 51 ppm is more consistent with the former as amino-boranes bound to one metal center show chemical shifts around 40–50 ppm,\cite{12,13,22,24,25} while bridging borylenes\cite{22} are generally observed between 90 and 100 ppm.\cite{23,33}

To probe the bonding of the amino-borane ligand in 4, DFT calculations were used as the basis for a Quantum Theory of Atoms in Molecules (QTAIM) analysis of the total electron density. The results are presented in Figure 2A, along with selected bond critical point (BCP) metrics. Figure 2B provides comparative BCP data for the bridging borylene complex C, the hydridoborate complex D, and [(PPh\(_3\))\(_2\)Rh(H)(\mu-H)(\mu-Cl),Rh(H)(PPh\(_3\))\(_2\)].\cite{34} C, a well-defined Rh\(_{III}\) dimer with both terminal and bridging hydrides.\cite{34} Average data are presented for all complexes where appropriate, although the discussion will focus on the bonding around a single rhodium center (Rh1).

In 4, the [Rh1/B1/H1] moiety displays bond paths between all three centers, and these enclose a ring critical point (RCP). Thus, 4 has direct Rh1–B1 and Rh1–H1 bonding interactions, while the B1–H1 bond is also intact. Comparison with the Rh1–B1 interaction in C provides similar \(\rho(\tau)\) and \(H(\tau)\) values, but highlights a much reduced bond ellipticity (\(\xi\)) of 0.08; this low value indicates dominant \(\sigma\)-bond character, whereas the value of 0.47 in 4 reflects the asymmetry introduced by the B1-H1 unit. In D, the absence of Rh-B BCPs confirms a lack of any direct Rh-B interaction, and this also reduces the average ellipticity of the Rh1–H1 and B1–H1 bonds. Also noticeable are the higher values of \(\rho(\tau)\) and \(H(\tau)\) for the terminal B1-H4 bond in D compared to the bridging B-H bonds in both that structure and, in particular, 4, all of which is consistent with a weakening of the latter. For E, the Rh1-H1 BCP has larger values for \(\rho(\tau)\) and \(H(\tau)\) than the Rh1-H1 BCP in 4, as well as a minimal \(\xi\) value. These data indicate a terminal Rh–H \(\sigma\)-bond and stress the differences in bridging character of H1 and H2 in 4. BCP data for the Rh1–H3–Rh2 bonds in 4, D, and E are very similar, suggesting that this moiety varies little across these three systems.

Taken together, the QTAIM analyses suggest that 4 is best described as a \(\mu\)-amino-borane Rh\(_1\) species; a \(\mu\)-borylene hydride Rh\(_{III}\) formulation can certainly be ruled out in light of the intact B1–H1/B1–H2 bonds and the lack of Rh1–H1/ Rh2–H2 terminal hydride character. The \(\mu\)-amino-borane ligand in 4 interacts with the rhodium centers through stretched B–H bonds that engage in strong Rh-H and Rh-B interactions. Further support for this assertion comes from the computed $\delta^{(11B)}$ chemical shifts (Figure 2) and the Pipek–Mezey localized orbitals, where a strong bonding interaction spanning all three Rh1, B1, and H1 centers was identified (see Figure 3).

The mechanism of the room temperature fluxional process observed for 4 was also probed with DFT calculations and a single transition state was found to account for this process (Scheme 4). This is accessed by cleavage of one (blue) B-H bond to give a transition state structure featuring two Rh-H-Rh bridging hydrides; movement of the original (red) Rh-H-Rh hydride into a Rh-H-B bridging position then completes the exchange (4'). Repeating this process from 4' exchanges a second B-H hydrogen (black) into the Rh-H-Rh bridging position (4''). The computed free energy of activation is 55.2 kJ mol\(^{-1}\), somewhat higher than the experimental value (39.2 ± 1.6 kJ mol\(^{-1}\)) but still consistent with facile room temperature exchange.

Understanding how bimetallic species such as 3 and 4 are formed, and subsequently react, is important for delineating...
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Determination of the resting state in catalysis was hampered by the addition of excess amine-borane (H₂B-NH₃ or H₂B-NMeH₂) to the preformed dimeric species 3 or 4 in THF, resulting in a mixture of products that have been resistant to characterization. Turning to the pure and well-characterized dimer 4, initial rate measurements in a closed system (4 mol% rhodium, THF) were more informative, and a first-order dependence for either H₂B-NH₃ or H₂B-NMeH₂, as well as catalyst 4, were measured for the early pseudo zero-order phase of catalysis (Supporting Information, Figures S19 and 20). Such behavior is not consistent with a rapid dimer–monomer equilibrium for which an order of 4[1] would be expected,[22,36,42] a view supported by the stoichiometric reactions with acetonitrile or toluene (see above). Under these conditions complexes 2 or 4 do not promote full conversion of amine-borane (for 4, 70% conversion of H₂B-NH₃ after 10 hrs). Informed by the sub-catalytic experiments and H₂ addition studies, we propose that [Rh₂(L̃)₄(μ-H₂)][BArF₄]₄[23] is formed during catalysis. Consistent with this hypothesis, isolated [Rh₂(L̃)₄(μ-H₂)][BArF₄] is a poorer catalyst for H₂B-NH₃ dehydrocoupling in a sealed system (4 mol% [Rh], 30% conversion after 10 hrs) than both 2 and 4. Interestingly, degassing the closed system restarted catalysis, indicating that inhibition by the H₂ formed during dehydrocoupling is partially reversible (Supporting Information, Figure S10). Co-promotion of dehydrocoupling by boronium is discounted, as these studies show that isolated 4 is an active pre-catalyst in its absence. Consistent with this statement, dehydrocoupling of H₂B-NH₂ is not catalyzed by [Et₂O-BH₂-NH₂][BArF₄] under the conditions used here (0.5 mol %, THF, 298 K, 3 hrs).[19] Overall, these observations do not let us discriminate between active catalysts derived from dimeric 4 (or 3) or monomeric species that result from irreversible, but fast, consumption of 4 (or 3), under the conditions of excess amine-borane.[18]

The ambiguity surrounding mono/bimetallic catalysis has parallels with xanthphos-based amine-borane dehydropolymerization catalysts, where P-C activated phosphido-bridged species are formed that are also active catalysts, in contrast to the amino-borane-bridged dimers observed here.[15] Deconvoluting these systems under conditions of high amine-borane concentration is thus a significant challenge to address if precise control over the resulting polyamino-borane is to be achieved by metal/ligand design. Nevertheless, the observation of novel and unexpected bridging amino-borane complexes as the first-formed species, offers tantalizing clues as to the nature of the actual catalysts; and also suggests that boronium cations may play a more general role in amine-borane dehydrocoupling than generally appreciated.[17,19]

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References


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The Simplest Amino-borane \( \text{H}_3\text{B} = \text{NH}_2 \) Trapped on a Rhodium Dimer: Pre-Catalysts for Amine-Borane Dehydropolymerization

Bridges of boron: Mechanistic investigations show that rhodium dimers bridged by amino-borane can form by a boronium-mediated route starting from amine–borane. These types of complexes are pre-catalysts for amine-borane dehydropolymerization, suggesting a possible role for bimetallic motifs in catalysis.