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Amine–Borane Dehydropolymerization

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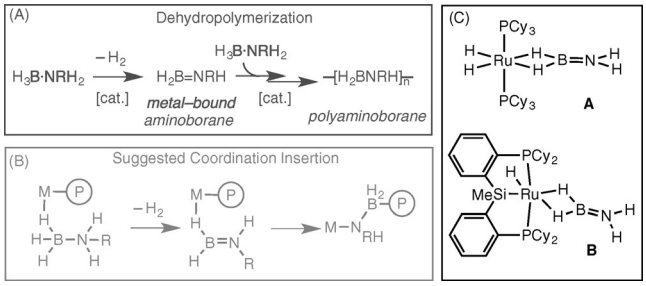
The Simplest Amino-borane $H_2B{=}NH_2$ Trapped on a Rhodium Dimer: Pre-Catalysts for Amine–Borane Dehydropolymerization

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

Abstract: *The μ-amino–borane complexes $[Rh_2(L^R)_2(\mu\text{-}H)(\mu\text{-}H_2B{=}NHR')][BAr^F{}_4]$ ($L^R{=}R_2P(CH_2)_3PR_2$; $R = Ph$, ^iPr; $R' = H$, Me) form by addition of $H_3B{\cdot}NMeR'H_2$ to $[Rh(L^R)(\eta^6\text{-}C_6H_5F)][BAr^F{}_4]$. 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 catalysis.*

Polyamino-boranes ($[H_2BNRH]_n$) are potentially exciting new materials that are isoelectronic with technologically pervasive polyolefins, but are chemically distinct because of (δ−)HB−NH(δ+) polarization. They are formed by the dehydropolymerization of amine-boranes ($H_3B{\cdot}NRH_2$; R = H or Me, for example; Scheme 1 A),[1] and metal-catalyzed routes to polyamino-boranes offer the potential for fine control over molecular weight and polymer stereochemistry.



Scheme 1. A) Amine-borane dehydropolymerization; B) a suggested coordination/insertion mechanism, P = polymer chain; C) examples of $H_2B{=}NH_2$ 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 ($H_2B{=}NRH$), and 2) subsequent B−N bond formation.[2–6] For some systems a coordination/insertion mechanism is proposed, although the precise structure of the propagating species is currently unresolved (Scheme 1 B).[3,5,6] 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 ($H_2C{=}CH_2$), which is stable under ambient conditions, the isoelectronic amino-borane ($H_2B{=}NH_2$) 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, $H_2B{=}NMeH$[9] or $H_2B{=}N^tBuH$[10] can be observed as transient species using in situ NMR spectroscopy before they also oligomerize. There are two examples where unstable $H_2B{=}NH_2$ can be trapped by coordination to a single metal center. These originate after dehydrogenation of a putative σ-ammonia borane[11] complex, forming $Ru(PCy_3)_2(H)_2(\eta^2\text{-}H_2B{=}NH_2)$ **A**[12] and (Cy-PSiP)-$Ru(H)(\eta^2\text{-}H_2B{=}NH_2)$ **B**, Cy-PSiP = κ^3-$(Cy_2PC_6H_4)_2SiMe$).[13]

We now report that $H_2B{=}NH_2$ can be trapped by a bimetallic $[Rh_2(R_2PCH_2CH_2CH_2PR_2)_2]^{2+}$ 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 $H_3B{\cdot}NH_3$ to a $[D_8]$THF solution of $[Rh(L^{Ph})(\eta^6\text{-}C_6H_5F)][BAr^F{}_4]$ **1** ($L^{Ph} = Ph_2P(CH_2)_3PPh_2$, $Ar^F = 3,5\text{-}(CF_3)_2C_6H_3$) 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 $[Rh_2(L^{Ph})_2(\mu\text{-}H)(\mu\text{-}H_2B{=}NH_2)][BAr^F{}_4]$ **3**. One equivalent of the boronium[9,17–20] cation $[THF{\cdot}BH_2{\cdot}NH_3][BAr^F{}_4]$ was also formed ($\delta(^{11}B)$ 0.5 (t), $J_{BH} = 108$ Hz; lit.[19] $[Et_2O{\cdot}BH_2{\cdot}NH_3][BAr^F{}_4]$ $\delta(^{11}B)$ 0.2, $J_{BH} = 125$ Hz).

In situ solution NMR data for **3** show a signal at $\delta(^{11}B)$ 51.5, a single ^{31}P environment ($\delta(^{31}P)$ 18.2, $J_{RhP} = 142$ Hz), and a broad peak at $\delta(^1H)$ −7.45 (integral ca. 3H relative to the

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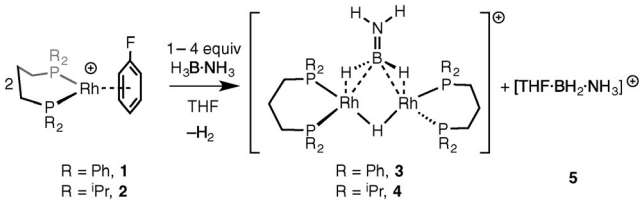
phenyl groups). ESI-MS shows a mono-cation at $m/z = 1060.16$ (calcd 1060.16) with the correct isotope pattern. Crystallization (THF/pentane/-18 °C) gave a small number of crystals, for which a single-crystal X-ray diffraction study showed a $H_2B{=}NH_2$ unit bridging a $\{(Rh_2(L^{Ph})_2(\mu\text{-}H)\}$ unit (Supporting Information, Figure S21). However, insufficient material was obtained upon 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 $[Rh(L^{Ph})(THF)_2][BAr^F{}_4]$ **6** was present in approximately 30 % yield.[21] To put the structure and spectroscopic data on a firm footing, the equivalent reaction using the ^{i}Pr-substituted chelating phosphine gave complex **4**, $[Rh_2(L^{iPr})_2(\mu\text{-}H)(\mu\text{-}H_2B{=}NH_2)][BAr^F{}_4]$, and **5** (Scheme 2).



Scheme 2. Formation of amino-borane coordinated dimers **3** and **4**. $[BAr^F{}_4]^-$ anions are not shown.

This reaction was slower than that observed for L^{Ph}. 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 $H_3B{\cdot}NH_3$, complex **4** is stable for at least two days in $[D_8]$THF solution. However, when formed in situ **4** decomposes over 24 hrs into a mixture of products, one of which can be characterized as $[Rh_2(L^{iPr})_2(H)_2(\mu\text{-}H)_3][BAr^F{}_4]$.[22] The room temperature solution NMR data obtained for **4** are very similar to those for **3**: $\delta(^{11}B)$ 51.1; $\delta(^{31}P)$ 40.8, $J_{RhP} = 142$ Hz; $\delta(^1H)$ −8.64 (3 H, broad). Progressive cooling to 180 K splits the high field hydride resonance into two signals, in a 2:1 ratio; while two ^{31}P environments were also observed, suggesting a fluxional process at room temperature. An Eyring plot yields the activation data: $\Delta H^{\ddagger} = 31.1 \pm 1.3$ kJ mol^{-1}, $\Delta S^{\ddagger} = -27 \pm 1$ J K^{-1} mol^{-1}, $\Delta G(298\text{ K})^{\ddagger} = 39.2 \pm 1.6$ 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 1 A. A dimeric Rh_2 unit is accompanied by one $[BAr^F{}_4]^-$ anion, confirming that it is a mono-cation. Two $\{Rh(L^{iPr})\}^+$ fragments are bridged by a hydride and a $H_2B{=}NH_2$ 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 $[Ir(PCy_3)_2(H)_2(H_2B{=}NMe_2)][BAr^F{}_4]$[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

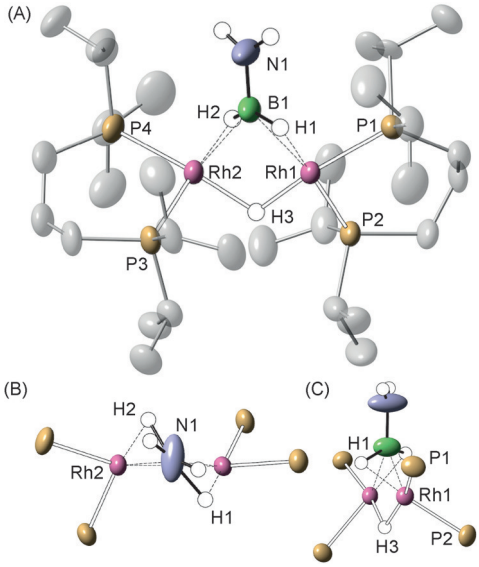
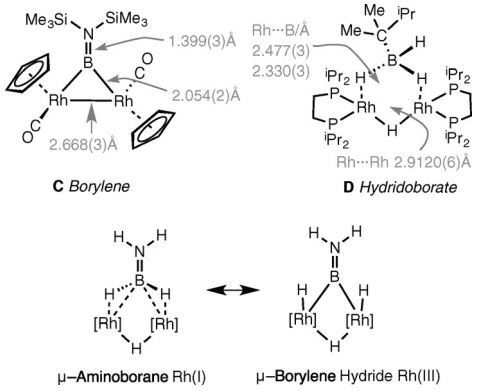


Figure 1. Solid-state structure of the cationic portion of complex **4**. Displacement ellipsoids are shown at the 50 % probability level. Selected bond distances (Å) and angles (°): Rh1···Rh2, 2.7874(4); Rh1–B1, 2.070(5); Rh2–B1, 2.055(5); B1–N1 1.377(6); P1–Rh1, 2.2550(10); P2–Rh1, 2.3063(10); Rh1–H1, 1.718; Rh2–H2, 1.723; ∡plane (N1B1H1H2)/plane (N1B1Rh1Rh2), 54.1; ∡plane (Rh1P1P2)/plane (Rh2P3P4), 100.2; ∡$(NH_2)/(BH_2)$ 24.3°.



Scheme 3. Limiting valence bond descriptions for complex **4**, and examples of bridging hydridoborate and borylene complexes. [Rh] = $\{Rh(L^{iPr})\}$, charge not shown.

distances suggest lengthened, but unbroken bonds (for example, 1.360 Å). The NH_2 group is slightly twisted with respect to the BH_2 group (24.3°; Figure 1 B). The whole $H_2B{=}NH_2$ 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 1 C). 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 Rh^I, with no M–M bond.[26] The end-on $\{Rh_2(\mu\text{-}H_2B{=}NH_2)\}$ binding mode contrasts with $H_2C{=}CH_2$ that bridges two metal centers symmetrically using both

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carbon atoms, in either μ-η^2:η^2 or μ-η^1:η^1 bonding modes,[27,28] highlighting the differences between these isosteres.[29]

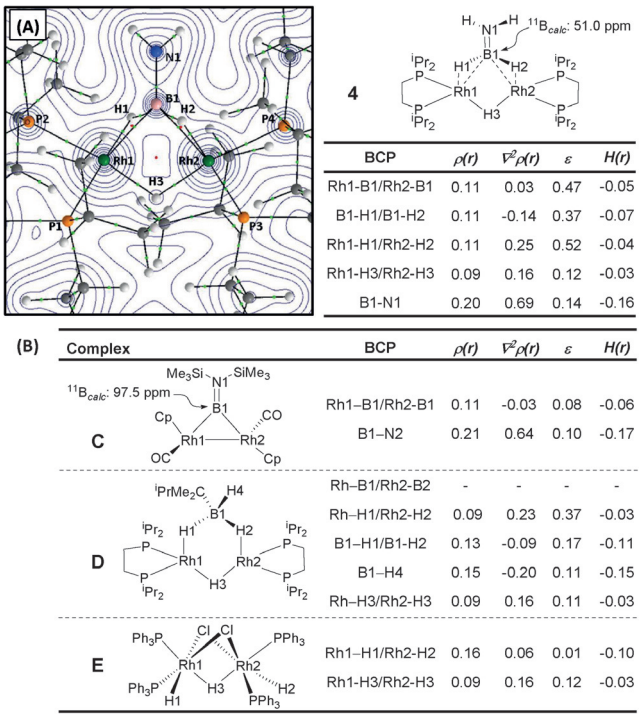
Surprisingly, the amino-borane in **4** is quite strongly bound. It is only slowly displaced by excess acetonitrile (7% in 50 min) to give a mixture of species, one of which is $[Rh(L^{iPr})(NCMe)_2][BAr^F_4]$.[22] No reaction occurs with toluene, which might be expected to form a $[Rh(L^{iPr})(\eta^6\text{-}C_6H_5Me)]^+$ complex if a monomeric $\{Rh(L^{iPr})\}^+$ fragment were accessible.[30] Addition of cyclohexene, shown to be a probe for free $H_2B{=}NH_2$,[2] gave no reaction. In contrast, H_2 rapidly reacts with **4** to form $[Rh_2(L^{iPr})_2(H)_2(\mu\text{-}H)_3][BAr^F_4]$.[22]

There are two limiting forms for the structure of **4** (and quasi-isostructural **3**): 1) a bridging amino-borane at two Rh^I centers, or 2) a bridging borylene dihydride (Rh^{III}), Scheme 3. The observed $\delta(^{11}B)$ 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,[12,13,24,31] while bridging borylenes[32] are generally observed between 90 and 100 ppm.[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 2 A, along with selected bond critical point (BCP) metrics. Figure 2 B provides comparative BCP data for the bridging borylene complex **C**, the hydridoborate complex **D**, and $[(PPh_3)_2Rh(H)(\mu\text{-}H)(\mu\text{-}Cl)_2Rh(H)(PPh_3)_2]^+$, **E**, a well-defined Rh^{III} dimer with both terminal and bridging hydrides.[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 $\rho(r)$ and $H(r)$ values, but highlights a much reduced bond ellipticity (ε) of 0.08; this low value indicates dominant σ-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 $p(r)$ and $H(r)$ 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 $\rho(r)$ and $H(r)$ than the Rh1-H1 BCP in **4**, as well as a minimal ε value. These data indicate a terminal Rh–H σ-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 μ-amino-borane Rh^I species; a μ-borylene hydride Rh^{III} formulism 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 μ-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 $\delta(^{11}B)$ 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).



BCP	ρ(r)	∇²ρ(r)	ε	H(r)
Rh1-B1/Rh2-B1	0.11	0.03	0.47	-0.05
B1-H1/B1-H2	0.11	-0.14	0.37	-0.07
Rh1-H1/Rh2-H2	0.11	0.25	0.52	-0.04
Rh1-H3/Rh2-H3	0.09	0.16	0.12	-0.03
B1-N1	0.20	0.69	0.14	-0.16

Figure 2. A) Contour plot of the electron density of the central part of **4** presented in the {Rh1B1Rh2} plane with projected stationary points, bond paths, bond critical points (BCP; green), and ring critical points (RCP; red); the associated table shows selected BCP metrics (a.u.; average data for indicated bonds) and computed $\delta(^{11}B)$ chemical shifts. B) Calculated BCP metrics (a.u.; average data for indicated bonds) for comparator complexes **C** (including the computed ^{11}B chemical shift), **D** and **E** ($\rho(r)$ = electron density, $\nabla\rho(r)$ = Laplacian of electron density, ε = bond ellipticity, $H(r)$ = local energy density). All geometries are based on the crystallographically determined heavy atom positions with hydrogen atoms optimized with the BP86 functional. For a full summary of parameters see Figures S24–27 and associated Tables in the Supporting Information.

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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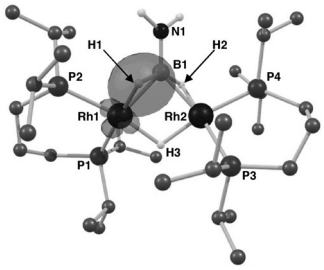
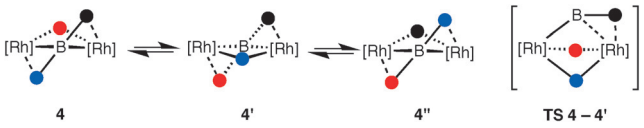
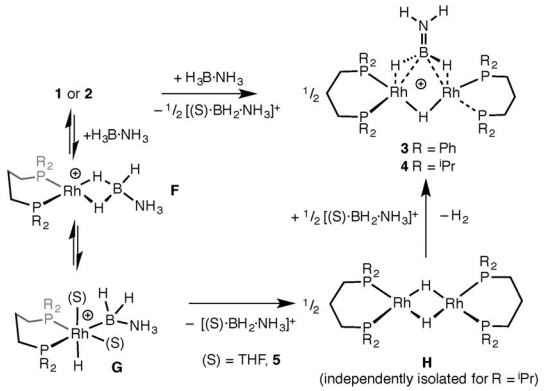


Figure 3. Pipek–Mezey localized orbital, highlighting the bonding interaction of the B1—H1 bond with center Rh1 (see Supporting Information, Figure S28, for details and related orbitals spanning the {Rh2B1H2} and {Rh1H3Rh2} moieties).



Scheme 4. Proposed fluxional process occurring in **4** (and **3**). Hydrogen atoms shown by filled circles. See Supporting Information for DFT calculated geometries and energies.

their role in amine-borane dehydrocoupling. The single equivalent of boronium $[THF{\cdot}BH_2{\cdot}NH_3][BAr^F{}_4]$ (**5**) formed indicates that a hydride abstraction route may be operating, as recently outlined by Conejero and co-workers for the dehydrocoupling of $H_3B{\cdot}NMe_2H$ by cationic $\{Pt\text{-}NHC\}^+$ catalysts,[17] as well as that occurring in cationic Ru/Ir-systems[35] or with $B(C_6F_5)_3$.[19] We reasoned that a similar process would yield **5** by B-H activation[16] and subsequent attack by THF (Scheme 5), alongside $\{Rh(L^R)H\}$



Scheme 5. Mechanism of formation of **3** and **4** by boronium protonation of neutral dimer **H**. (S) = THF or Et_2O. $[BAr^F{}_4]^-$ anions are not shown.

that would dimerize to give neutral $[Rh(L^R)H]_2$ (for example, complex **H**). Subsequent protonation[17] by boronium **5** and elimination of H_2 would give $H_2B{=}NH_2$ trapped on a rhodium dimer. To test this hypothesis, addition of **5** to the neutral dimer is required. $[Rh(L^{Ph})H]_2$ is unknown, and our attempts to prepare it have not been successful. $[Rh(L^{iPr})H]_2$ is a known complex, first prepared by Fryzuk in 1989,[36] and addition of one equivalent of the known boronium salt $[Et_2O{\cdot}BH_2{\cdot}NH_3][BAr^F{}_4]$[19] to $[Rh(L^{iPr})H]_2$ in Et_2O solvent, resulted in the immediate formation of **4** and gas evolution (H_2), which is consistent with the mechanism shown.

A dimeric species similar to **3** was also formed when one equivalent of $H_3B{\cdot}NMeH_2$ was added to **1** in THF solution. This was characterized by in situ NMR spectroscopy and ESI-MS as $[Rh_2(L^{Ph})_2(\mu\text{-}H)(\mu\text{-}H_2B{=}NMeH)][BAr^F{}_4]$ **8**: $\delta(^1H)$ −6.84; $\delta(^{31}P\{^1H\})$ 22.2, 21.5; $\delta(^{11}B)$ 50.6.[21] $[THF{\cdot}BH_2{\cdot}NMeH_2][BAr^F{}_4]$ was also formed ($\delta(^{11}B)$ 2.8 (t), $J_{HB} = 123$ Hz; lit. Et_2O adduct $\delta(^{11}B, CD_2Cl_2)$ 1.7 (t), $J_{HB} = 121$ Hz[9]). A more complex mixture of species was formed with $H_3B{\cdot}NMe_2H$, suggesting steric factors may be important in the formation of these aminoborane dimers, although a signal observed at $\delta(^{11}B)$ 52.7 suggests dimer formation. Complexes **3**, **4**, and **8** presumably form via a σ-complex $[Rh(L^R)(H_3B{\cdot}NRH_2)][BAr^F{}_4]$, R = H (**F** Scheme 5) or Me. In THF solution, using the L^{Ph} ligand, these σ-complexes were not observed as boronium formation and subsequent formation of **3** is fast. For L^{iPr}, an intermediate σ-complex could be observed on the way to **4**, $[Rh(L^{iPr})(H_3B{\cdot}NH_3)][BAr^F{}_4]$, presenting NMR data consistent with structure **F**.[21] Using $H_3B{\cdot}NMe_3$ (in which the N—H bonds are absent) $[Rh(L^{iPr})(H_3B{\cdot}NMe_3)][BAr^F{}_4]$ (**7**) was isolated and structurally characterized, confirming the in situ NMR studies (Supporting Information, Figure S23). The rapid reaction of $[Et_2O{\cdot}BH_2{\cdot}NH_3][BAr^F{}_4]$ with $[Rh(L^{iPr})H]_2$ to form **4** suggests protonation is not slow for this system; currently we cannot determine whether B—H activation or boronium formation is the rate limiting process, although it is likely that either could be promoted by excess amine-borane via N-H···H-B interactions.[37] Calculations on the $\{Pt\text{-}NHC\}^+/H_3B{\cdot}NMe_2H$ system suggest boronium formation is rate limiting.[17]

Complex **1** (0.5 mol%, THF, 3 hrs, open system) promoted the dehydrocoupling of $H_3B{\cdot}NH_3$ (1.2 equiv of H_2 evolved by gas burette; Supporting Information, Figures S4–S7) to form oligomeric species such as *B*-(cyclotriborazanyl)amine-borane (BCTB),[3,38] and insoluble polyaminoborane.[3] With more soluble $H_3B{\cdot}NMeH_2$, polymethylamino-borane was formed $[H_2BNMeH]_n$, which was isolated by precipitation from hexanes ($M_w = 30\,600$ g mol^{-1}, $Đ = 2.6$), alongside H_2 (1.1 equiv, gas burette). Consistent with the rapid formation of dimers such as **8** in THF, no induction period was observed (as measured by H_2 evolution) and similar TOF values were recorded (ca. 200 hr^{-1} for 1 equiv H_2), starting from monomeric **1** or in situ formed dimeric **8** (Scheme 6).[39] Changing the solvent to non-nucleophilic 1,2-$F_2C_6H_4$, and using **1** or in situ generated **8** as a catalyst, did not present an induction period and also revealed a faster TOF (for **8**, ca. 1000 hr^{-1} with 1 equiv of H_2 released).[40] Sub-catalytic in situ experiments in this solvent[21] show that dimer **8**, $[(BH_2)_2NMeH(\mu\text{-}H)]$ and boronium $[(NH_2Me)_2BH_2][BAr^F{}_4]$ are present;[41] the latter is suggested to arise from $NMeH_2$ formed from B—N bond cleavage in $H_3B{\cdot}NMeH_2$.[17] Thus, it is likely that similar active species are present in THF or 1,2-$F_2C_6H_4$. The lack of induction period is in direct contrast to xantphos-based rhodium catalysts, which show induction periods for $H_3B{\cdot}NMeH_2$ dehydrocoupling in C_6H_5F,[5,15] suggesting that a different kinetics regime or mechanism is in operation.

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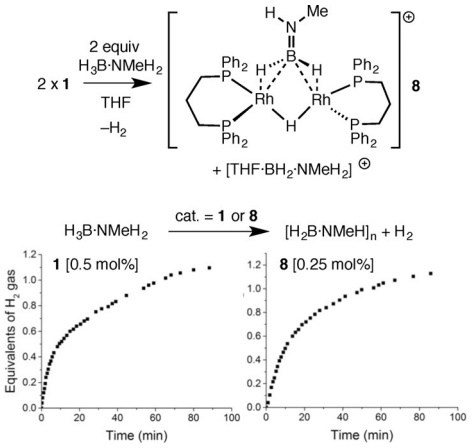

Scheme 6. H_2 evolution experiments using **1** or **8**, and $H_3B{\cdot}NMeH_2$ (0.5 mol% [Rh], 0.41 M amine-borane, THF, 298 K). $[BAr^F{}_4]^-$ anions are not shown.

Determination of the resting state in catalysis was hampered by the addition of excess amine-borane ($H_3B{\cdot}NH_3$ or $H_3B{\cdot}NMeH_2$) 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 $H_3B{\cdot}NH_3$ or $H_3B{\cdot}NMeH_2$, 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 $[\mathbf{4}]^{1/2}$ 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 $H_3B{\cdot}NH_3$ after 10 hrs). Informed by the sub-catalytic experiments and H_2 addition studies, we propose that $[Rh_2(L^{iPr})_2(H)_2(\mu\text{-}H)_3][BAr^F{}_4]$[22] is formed during catalysis. Consistent with this hypothesis, isolated $[Rh_2(L^{iPr})_2(H)_2(\mu\text{-}H)_3][BAr^F{}_4]$ is a poorer catalyst for $H_3B{\cdot}NH_3$ 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 H_2 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 $H_3B{\cdot}NH_3$ is not catalyzed by $[Et_2O{\cdot}BH_2{\cdot}NH_3][BAr^F{}_4]$ 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.[43]

The ambiguity surrounding mono/bimetallic catalysis has parallels with xantphos-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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