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Development of a Generic Mechanism for the Dehydrocoupling of Amine-Boranes: A Stoichiometric, Catalytic, and Kinetic Study of $H_3B{\cdot}NMe_2H$ Using the $[Rh(PCy_3)_2]^+$ Fragment

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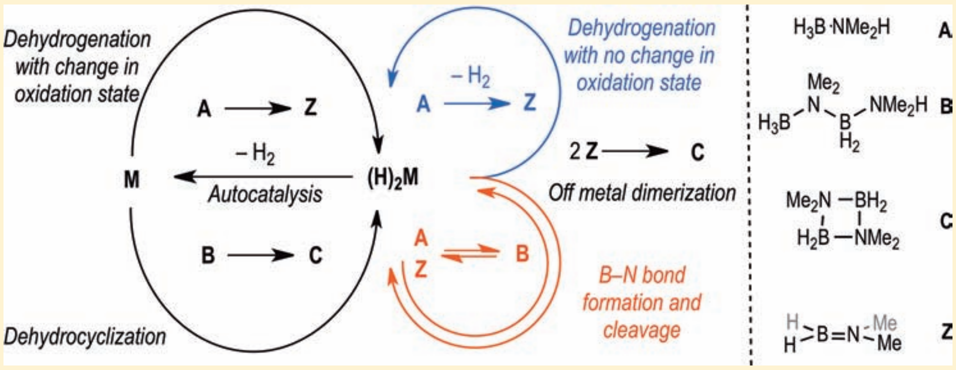
S *Supporting Information*



ABSTRACT: The multistage Rh-catalyzed dehydrocoupling of the secondary amine-borane $H_3B{\cdot}NMe_2H$, to give the cyclic amino-borane $[H_2BNMe_2]_2$, has been explored using catalysts based upon cationic $[Rh(PCy_3)_2]^+$ (Cy = cyclo-C_6H_{11}). These were systematically investigated (NMR/MS), under both stoichiometric and catalytic regimes, with the resulting mechanistic proposals for parallel catalysis and autocatalysis evaluated by kinetic simulation. These studies demonstrate a rich and complex mechanistic landscape that involves dehydrogenation of $H_3B{\cdot}NMe_2H$ to give the amino-borane $H_2B{=}NMe_2$, dimerization of this to give the final product, formation of the linear diborazane $H_3B{\cdot}NMe_2BH_2{\cdot}NMe_2H$ as an intermediate, and its consumption by both B−N bond cleavage and dehydrocyclization. Subtleties of the system include the following: the product $[H_2BNMe_2]_2$ is a modifier in catalysis and acts in an autocatalytic role; there is a parallel, neutral catalyst present in low but constant concentration, suggested to be $Rh(PCy_3)_2H_2Cl$; the dimerization of $H_2B{=}NMe_2$ can be accelerated by MeCN; and complementary nonclassical BH···HN interactions are likely to play a role in lowering barriers to many of the processes occurring at the metal center. These observations lead to a generic mechanistic scheme that can be readily tailored for application to many of the transition-metal and main-group systems that catalyze the dehydrocoupling of $H_3B{\cdot}NMe_2H$.

1. INTRODUCTION

The transition-metal-catalyzed dehydrocoupling[1−3] of amine-boranes, prototypically $H_3B{\cdot}NH_3$, has attracted considerable interest due to the potential for controlled and rapid release of dihydrogen (hydrogen storage) or dehydropolymerization (the production of B−N polymeric materials).[4−11] The dehydrocoupling of the simplest congener, $H_3B{\cdot}NH_3$, is the most interesting with regard to the percentage of hydrogen stored. Recent progress in the regeneration of the spent fuel from this process is an exciting development in this area;[12−14] however, the resulting boron/nitrogen products (oligomers, polymers, borazines, cross-linked B/N materials) are often ill-defined and insoluble, meaning that following the reaction in a mechanistic sense is difficult, although significant progress has been made on this difficult problem.[3,9,15−17] The primary amine-borane $H_3B{\cdot}NMeH_2$ forms oligomeric and polymeric materials $[BH_2NMeH]_n$ on dehydrocoupling,[18] which again makes mechanistic studies less than straightforward. The next amine-borane in the homologous series $H_3B{\cdot}NMe_2H$ (**A**) nominally gives one final product on dehydrogenation, the soluble cyclic amino-borane dimer $[H_2BNMe_2]_2$ (**C**), while intermediates on the pathway to **C** are also soluble. This makes mechanistic investigations more straightforward. Because of this there are now a considerable number of main-group[19−22] and early-,[23−29] mid-,[30−38] and late-transition-metal[16,39−45] systems that have been found to mediate this transformation for **A**. Although heterogeneous (colloidal) were the first systems reported,[40,41] in general, homogeneous catalysts now dominate, with some notable recent exceptions.[46−48] Metal-promoted hydrolysis is also known.[49] Degenerate metal-free hydrogen transfer between amino-boranes and amine-boranes has

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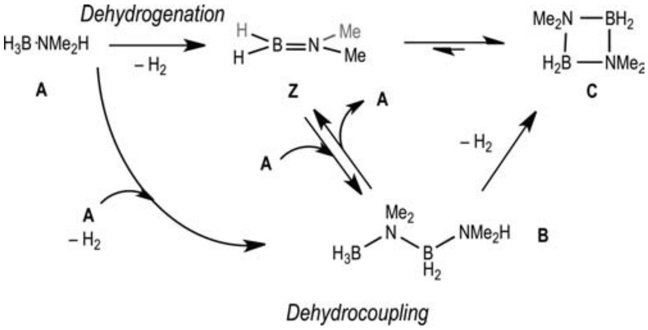
recently been reported, which adds additional detail to the overall dehydrogenation landscape.[50] A related, autocatalytic role for the metal-free production of amino-borane has been explored computationally.[37]

Scheme 1. Suggested Intermediates and Pathways for the Dehydrocoupling of $H_3B·NMe_2H$ Using Transition-Metal Catalysts[a]



[a]The role of the metal in each step is not given. Arrows indicate possible pathways, but not all pathways necessarily operate for each catalyst system.[28,34,47,51]

A number of mechanistic regimes, as identified by the intermediate boron−nitrogen species detected during dehydrocoupling in stoichiometric and kinetic studies, have been suggested[24,29,32−34,40,42,51−54] (Scheme 1): initial dehydrogenation of **A** to form the amino-borane $H_2B{=}NMe_2$ (**Z**); coupling of **A** and **Z**, or of two **A** (to also give H_2), to form the intermediate linear diborazane **B**; and formation of the dimeric final product **C** by either off-metal dimerization of **Z** or dehydrocyclization of **B**. Stoichiometric experimental studies have shown that amine-boranes can undergo dehydrogenation on a metal to give bound amino-boranes such as **Z**.[30,43,51,55,56] Although many studies assume rapid off-metal dimerization of **Z** to give **C**, it is only recently that the rate constant for this second-order process has been determined,[51] using a latent source of **Z** bound to a cationic $[Ir(PCy_3)_2H_2]^+$ center. This same study also reported the role of metal in the coupling of **Z** with **A** to give intermediate **B**. This also has relevance in the dehydropolymerization of primary amine-boranes, for which a metal-based coordination/insertion mechanism has been suggested.[18,50,57] These observations are also in agreement with earlier interpretations made using PNP−Ru systems.[34] Studies using Cp_2Ti catalysts indicate **B** is formed by a different route, by direct coupling of two **A**, followed by metal-centered dehydrocyclization to give **C**.[28] Interestingly, some systems do not appear to proceed via **B**, namely [Rh(chelating bisphosphine)]$^+$ [58] and photogenerated $CpFe(CO)_n$[31] or $Cr(CO)_4$.[24] With regard to dehydrogenation, specific catalysts can operate in an inner-sphere way, in which B−H oxidative addition/N−H transfer of a σ-bound amine-borane[59,60] is invoked (in either order) at the metal center only, or by cooperative metal−ligand reactivity.[30,61−64] Main-group systems (Ca, Mg,[19,20] Al[22]) proceed via a mechanism that points to N−H activation occurring first, and intermediates related to **B** have also been observed. Together, these studies show that the mechanism for dehydrocoupling of **A** is complex (even though there is nominally only one product, **C**) and is highly dependent on the metal catalyst.[7,9] In addition, observations indicate that the consumption of both **A** and intermediate **B** in the reaction is not a simple intramolecular process, with additional amine-borane required to promote/accelerate onward reactivity.[54,65,66]

What is lacking in this burgeoning field of catalysts that dehydrocouple $H_3B·NMe_2H$ is a unified model in which mechanistic clues can be placed in context. Here we present a detailed study of isolated intermediates, catalysis, stoichiometric reactivity, and kinetic simulation using the $[Rh(PCy_3)_2]^+$ catalyst system. These studies demonstrate a rich and complex mechanistic landscape that involves dehydrogenation of **A** to give the amino-borane **Z**, dimerization of this to give the final product **C**, formation of the linear diborazane **B** as an intermediate, and its consumption by both B−N bond cleavage and dehydrocyclization. Additional subtleties of the system include that the product $[H_2BNMe_2]_2$ is a modifier in catalysis and acts in an autocatalytic role; there is a parallel catalyst present in low concentration, suggested to be the neutral complex $Rh(PCy_3)_2H_2Cl$; the dimerization of $H_2B{=}NMe_2$ can be accelerated by MeCN; and complementary nonclassical BH···HN interactions are likely to play a role in lowering barriers to many of the processes occurring at the metal center. These observations lead us to propose a generic mechanistic scheme that can be readily tailored for application to many of the transition-metal and main-group systems that catalyze the dehydrocoupling $H_3B·NMe_2H$.

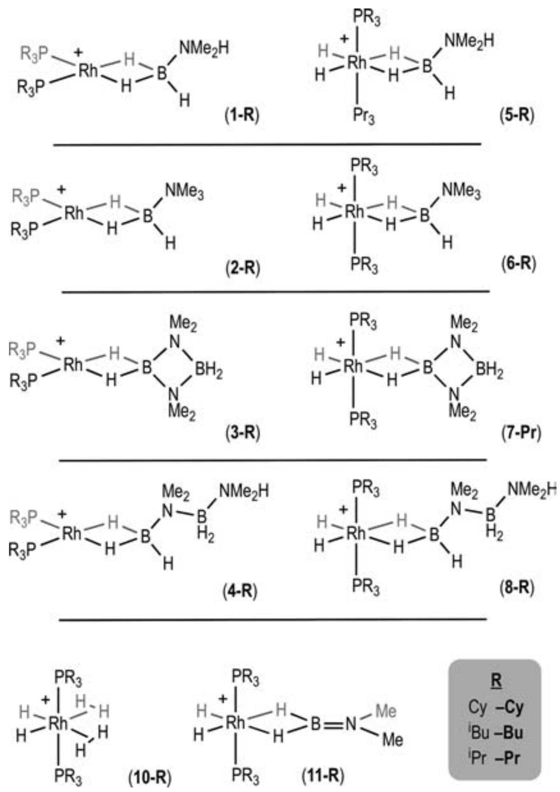
2. RESULTS

2.1. Choice of System.

We have recently reported the use of cationic $[Rh(PR_3)_2]^+$ and related fragments to study the dehydrocoupling of **A**.[51,53,54,58,65−69] These systems have an advantage of undergoing oxidative addition/reductive elimination processes,[70,71] form σ-complexes with amine-boranes (so-called unstretched Shimoi σ-complexes[59]), and are competent, if relatively slow, catalysts for the dehydrocoupling of **A**. A computational analysis of the first dehydrogenation step (i.e., **A**→**Z**) using the $[Rh(P^iBu_3)_2]^+$ fragment shows that a Rh(I)/Rh(III) cycle can operate (oxidative addition of B−H and N−H transfer).[54] Alternatively, a constant oxidation-state Rh(III) cycle, operating in a σ-CAM fashion,[72] is also possible. Calculations on the related $[Ir(PCy_3)_2H_2]^+$ system indicate a constant oxidation-state Ir(III) cycle also operates, but with a larger barrier, consistent with the experimentally observed slower rate of dehydrocoupling.[51] In all these studies, N−H activation is shown to be a higher energy process than B−H activation, an observation supported by experimental data.[51,54,68] Chart 1 shows σ-amine-borane and amino-borane complexes, pertinent to this work, that have been isolated or observed in situ.

We have previously reported that the $[Rh(P^iPr_3)_2]^+$ fragment mediates the dehydrocoupling of **A** more slowly than $[Rh(P^iBu_3)_2]^+$ does,[53] while in systems such as $[Rh(Ph_2PCH_2CH_2CH_2PPh_2)]^+$, with chelating ligands, turnover is 2 orders of magnitude faster[58] (ToF = 4 h^{-1}, versus 15 h^{-1}, versus 1250 h^{-1} respectively in a system open to Ar). We now screened a number of additional $[Rh(PR_3)_2]^+$ fragments, settling on the $[Rh(PCy_3)_2]^+$ system (Cy = cyclohexyl) as offering an appropriate rate for studying the reaction kinetics, lying between ^iPr and ^iBu. Monitoring reactions by ^{11}B NMR spectroscopy (vide infra) shows a similar reaction profile for all three $[Rh(PR_3)_2]^+$ fragments (R = Cy, ^iPr, and ^iBu): with **A** consumed, **B** formed as an intermediate, and **C** the final product. The chelate systems are simply too fast for this study and have the additional complication of an induction period.[58]

Chart 1. Rh(I) and Rh(III) Amine- and Amino-Borane Complexes Discussed in This Paper[a]

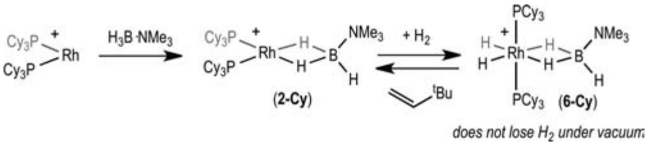


[a] $[\mathrm{BAr^F{}_4}]^-$ anions not shown. R = ^{i}Bu;[54,67] ^{i}Pr;[53,73,74] **10-Cy**;[74] **11-Cy**.[69] Other R = Cy complexes are from this work.

A suitable starting point for studying both the stoichiometric and catalytic transformations in our previous studies has been complexes of the general formula $[\mathrm{Rh(PR_3)_2}(\eta^6\text{-}\mathrm{C_6H_5F})][\mathrm{BAr^F{}_4}]$ ($\mathrm{Ar^F = C_6H_3(CF_3)_2}$), in which the fluorobenzene ligand is easily substituted.[53,54,58] We have been unable to isolate the equivalent complexes using the $\mathrm{PCy_3}$ ligand, presumably due to steric bulk coupled with the lability of the fluorobenzene ligand. The $[\mathrm{Rh(PCy_3)_2}][\mathrm{BAr^F{}_4}]$ precatalyst was instead generated in situ from addition of $\mathrm{Na[BAr^F{}_4]}$ to a 1,2-$\mathrm{C_6H_4F_2}$ solution of $[\mathrm{Rh(PCy_3)_2Cl}]_2$,[75] and is presumed to give $[\mathrm{Rh(PCy_3)_2}L_n][\mathrm{BAr^F{}_4}]$ (L_n = solvent or agostic interaction) which can react readily with Lewis bases, such as amine-boranes. Addition of $\mathrm{H_2}$ (4 atm) to this solution of $[\mathrm{Rh(PCy_3)_2}L_n][\mathrm{BAr^F{}_4}]$ immediately gives the known Rh(III) bis-hydride bis-dihydrogen complex $[\mathrm{Rh(PCy_3)_2H_2(H_2)_2}][\mathrm{BAr^F{}_4}]$ (**10-Cy**) quantitatively to the detection limits of $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectroscopy (approximately 95%).[74] Initial screening of the dehydrogenation of **A** using this catalyst showed that both the rate of overall reaction and time/concentration plots were qualitatively similar to those obtained when using $[\mathrm{Rh(P^iPr_3)_2}(\eta^6\text{-}\mathrm{C_6H_5F})][\mathrm{BAr^F{}_4}]$[53] or $[\mathrm{Rh(P^iPr_3)_2Cl}]_2/\mathrm{Na[BAr^F{}_4]}$, and we thus reasoned that the NaCl co-product had no part to play. However, as our studies revealed, this is not the case, and small amounts of chloride ion do appear to be important.

2.2. Reactivity with $\mathrm{H_3B{\cdot}NMe_3}$. Our initial studies used $\mathrm{H_3B{\cdot}NMe_3}$ as the amine-borane substrate. As this has no N−H functional group, it does not undergo dehydrocoupling and thus serves to provide baseline reactivity and spectroscopic studies. Addition of $\mathrm{H_3B{\cdot}NMe_3}$ to $[\mathrm{Rh(PCy_3)_2}L_n][\mathrm{BAr^F{}_4}]$ rapidly (on mixing) forms purple $[\mathrm{Rh(PCy_3)_2}(\eta^2\text{-}\mathrm{H_3B{\cdot}NMe_3})][\mathrm{BAr^F{}_4}]$ (**2-Cy**) that has been characterized spectroscopically by comparison with $\mathrm{P^iBu_3}$ (**2-Bu**)[54] and $\mathrm{P^iPr_3}$ (**2-Pr**)[53] analogues (Scheme 2). Complex **2-Cy** is isolated as a lilac solid in 63% yield, although by NMR spectroscopy the reaction is quantitative. NMR data are in full accord with the formulation. Notably, a 34.4 ppm downfield shift is observed in the ^{11}B NMR spectrum for coordinated $\mathrm{H_3B{\cdot}NMe_3}$ (δ 27.1), compared with the free amine-borane ligand (δ −7.3), and a quadrupolar-broadened integral 3H signal in the ^{1}H NMR spectrum at δ −2.87, both indicative of three-center two-electron Rh−H−B interactions that are undergoing fast exchange on the NMR time scale between terminal B−H and B−H−Rh sites.[53,60,76,77] Addition of $\mathrm{H_2}$ to a 1,2-$\mathrm{C_6H_4F_2}$ solution of **2-Cy** results in the immediate formation of the colorless Rh(III) dihydride complex $[\mathrm{Rh(PCy_3)_2H_2}(\eta^2\text{-}\mathrm{H_3B{\cdot}NMe_3})][\mathrm{BAr^F{}_4}]$ (**6-Cy**), as characterized by NMR spectroscopy by comparison with **6-Bu**[54] and **6-Pr**.[53] Reductive elimination of $\mathrm{H_2}$ from **6-Cy** to give **2-Cy** does not occur easily, as placing **6-Cy** under a vacuum (2×10^{-2} mbar) results in no change, and only on addition of the hydrogen acceptor *tert*-butylethene (tbe) is the Rh(I) complex **2-Cy** re-formed. This is similar to **6-Pr**, but is unlike **6-Bu** in which $\mathrm{H_2}$ loss occurs in solution under an Ar flush. These differences may be related to the relative steric influences of the phosphine ligands, as P−Rh−P bite angle effects[78] and agostic interactions[79] have both been shown to promote $\mathrm{H_2}$ loss.

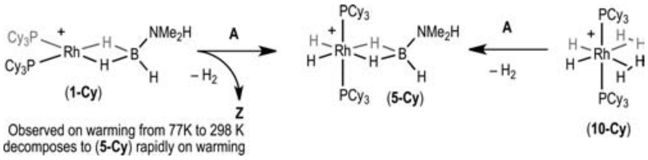
Scheme 2[a]



[a] $[\mathrm{BAr^F{}_4}]^-$ anions are not shown.

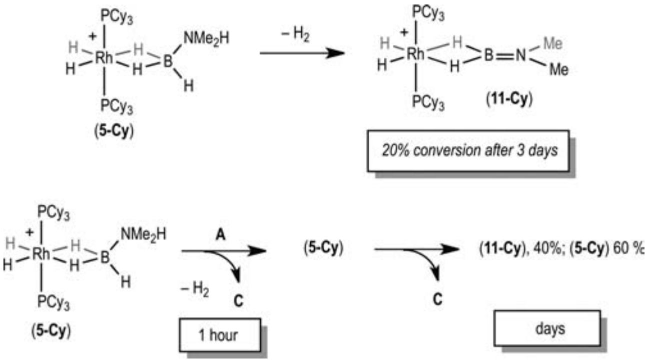
2.3. Reactivity with $\mathrm{H_3B{\cdot}NMe_2H}$: Rh(I) and Rh(III) Complexes. As for $\mathrm{H_3B{\cdot}NMe_3}$, addition of approximately 1 equiv of **A** to $[\mathrm{Rh(PCy_3)_2}L_n][\mathrm{BAr^F{}_4}]$ rapidly forms purple $[\mathrm{Rh(PCy_3)_2}(\eta^2\text{-}\mathrm{H_3B{\cdot}NMe_2H})][\mathrm{BAr^F{}_4}]$ **1-Cy**. However, unlike **2-Cy**, **1-Cy** is not stable in solution and quickly (complete consumption in 5 min on warming from 77 to 298 K) forms the Rh(III) complex $[\mathrm{Rh(PCy_3)_2H_2}(\eta^2\text{-}\mathrm{H_3B{\cdot}NMe_2H})][\mathrm{BAr^F{}_4}]$ (**5-Cy**), as characterized by analogy with **5-Bu**.[54] Conversion to **5-Cy** proceeds to ~50% ($^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectroscopy), with the amino-borane complex $[\mathrm{Rh(PCy_3)_2H_2}(\eta^2\text{-}\mathrm{H_2B{=}NMe_2})][\mathrm{BAr^F{}_4}]$ (**11-Cy**) also formed (~25%), alongside an unidentified Rh−phosphine complex that does not appear to have hydrides or a bound borane [^{1}H and $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectroscopy, ~25%, δ ^{31}P = 47.8, J(RhP) = 118 Hz]. No free **Z** or **C** was observed under these conditions. Complex **1-Cy** was characterized by analogy with its ^{i}Bu analogue[54] via rapidly freezing a 1,2-$\mathrm{C_6H_4F_2}$ solution of the reactants and warming to 298 K in the NMR probe. Use of 2 equiv of **A** resulted in an even shorter-lived **1-Cy**, less than 10% being observed after 1 min of warming from 77 to 298 K (Scheme 3). Under these conditions **Z** is observed as an intermediate, which proceeds to form **C**.[51,80] Over an extended time (days) **5-Cy** slowly converts to **11-Cy**. Complex **11-Cy** has been previously isolated from the retro-dimerization of **C** trapped by the $[\mathrm{Rh(PCy_3)_2H_2}]^+$ fragment,[51] while **11-Bu** has been observed as the final organometallic product at the end of catalytic dehydrogenation of **A** using $[\mathrm{Rh(P^iBu_3)_2}][\mathrm{BAr^F{}_4}]$.[54] The $\mathrm{H_2B{=}N^iPr_2}$ analogue has also been recently reported.[69]

Scheme 3[a]



[a] $[BAr^F_4]^-$ anions are not shown.

Scheme 4[a]



[a] $[BAr^F_4]^-$ anions are not shown.

Addition of **A** to a solution of the Rh(III) bis-dihydrogen bis-dihydride complex **10-Cy**, formed in situ, also results in the formation of pale yellow **5-Cy** in quantitative yield by NMR spectroscopy.

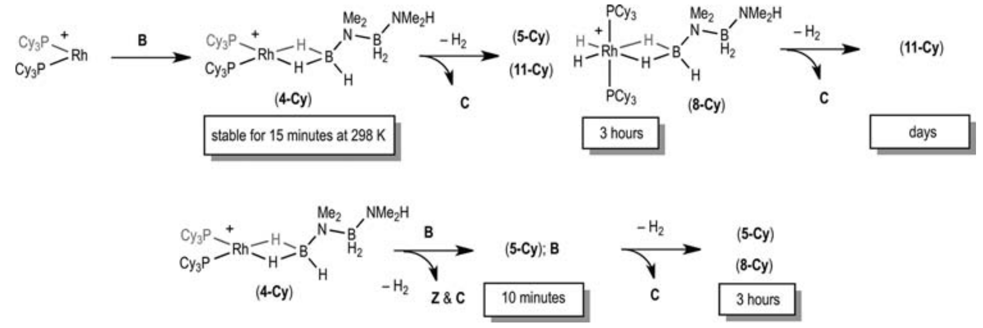
5-Cy does not lose H_2 when placed under a vacuum. In the absence of excess **A**, complex **5-Cy** is also relatively stable, with only 20% conversion to **11-Cy** observed after 3 days (Scheme 4). However, addition of a further 1 equiv of **A** to **5-Cy** results in the complete conversion of **A** to **C** after 1 h, during which time **Z** is observed as an intermediate. **5-Cy** is the only organometallic species observed in solution during this time. After 24 h, NMR spectroscopy shows **5-Cy** and **11-Cy** to be present in approximately equal proportions, alongside **C**.

These results reveal a number of important observations pertinent to the overall mechanism. First, dehydrogenation of bound **A** on the cationic Rh(I) center to form a cationic Rh(III) dihydride and **Z** is rapid. In contrast, the Rh(III) complex **5-Cy** turns over much more slowly, and only to any appreciable extent when excess **A** is present. Under these conditions, H_2 elimination from **5-Cy** to give **1-Cy** is negligible. The cationic Rh(I)/Rh(III) dehydrogenation manifold thus appears to be fast, while the Rh(III) manifold is considerably slower. The cationic Rh(III) species will thus form quickly, and pool, during catalysis. This is consistent with calculations that show **5-Bu** and **11-Bu** to be rather stable[54] and that **5-Cy** is observed as the resting state during catalysis (vide infra). Observations on Rh(chelate) systems which favor the Rh(I) oxidation state, and which are extremely efficient catalysts for the dehydrogenation of **A** to ultimately form **C**, support this observation.[58] The inverse dependence on the lifetime of **1-Cy** with increasing concentrations of **A**, as well as that turnover in dehydrogenation of **5-Cy** requires added **A**, suggests that an additional molecule of **A** must also be involved in these dehydrogenation processes, possibly via outer-sphere B−H···H−N intermolecular interactions.[81,82] Such interactions are being increasingly recognized as important for lowering barriers in H_2 loss and oligomerization processes in amine-boranes[37,83−85] and related complexes,[86] and have previously been suggested to occur on the basis of stoichiometric and catalytic studies on other metal-based systems.[54,57,65,66] Barriers to metal-based dehydrogenation might be lowered by such outer-sphere interactions.[87] We have recently reported such interactions between two σ-coordinated amine-boranes on a Rh(I) metal center. Further studies, however, indicated that these *intra*molecular BH···HN bonds do not undergo simple dehydrogenation,[38,65] and that a more complex mechanism is probably operating.[66]

2.4. Reactivity with Linear Dimer $H_3B·NMe_2BH_2·NMe_2H$, Rh(I) and Rh(III). The linear diborazane $H_3B·NMe_2BH_2·NMe_2H$ (**B**) has been observed as an intermediate during catalysis using rhodium P^iBu_3[54] and P^iPr_3[53] complexes. It has also been implicated as an intermediate in other systems,[28,34,40,42,51,66] although, interestingly, there are also catalyst systems where it has been shown not to be an intermediate.[31,58] Experimental observations suggest that **B** is formed in a metal-centered process that involves metal-bound **Z**,[34,51] while coordination of an amino-borane to a metal center being a requirement for B−N bond formation has recently been suggested in studies on the oligomerization (dehydropolymerization) of $H_3B·NMeH_2$.[50,57]

Addition of approximately 1 equiv of **B** to in situ generated $[Rh(PCy_3)_2L_n][BAr^F_4]$ rapidly forms purple $[Rh(PCy_3)_2(\eta^2\text{-}H_3B·NMe_2BH_2·NMe_2H)][BAr^F_4]$ (**4-Cy**). This is the only species observed at room temperature by NMR spectroscopy over a period of 15 min (Scheme 5). Characterization of **4-Cy** was based on comparison of data with those previously reported for **4-Bu**.[54] The relative stability of **4-Cy** is in sharp contrast to that of **1-Cy**; the latter is only observed as a

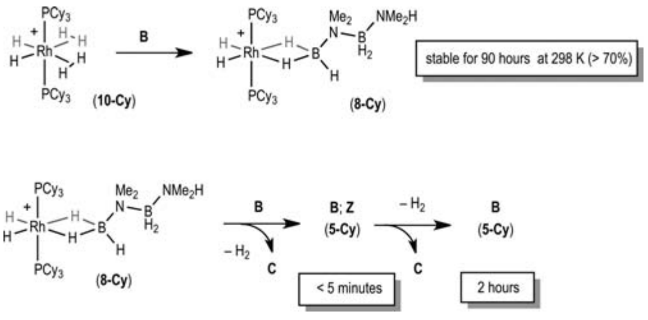
Scheme 5[a]



[a] $[BAr^F_4]^-$ anions are not shown.

transient intermediate, en route to Rh(III) complex **5-Cy**, even at low temperature. Over time in solution **4-Cy** slowly converts to a mixture of Rh(III) complex **5-Cy**/**11-Cy** and [Rh(PCy$_3$)$_2$H$_2$(η^2-H$_3$B·NMe$_2$BH$_2$·NMe$_2$H)][BAr$^F{}_4$] (**8-Cy**), with 90% consumption of **4-Cy** after 3 h. After a period of days, the solution predominantly contains **11-Cy** (85%), with **C** as the only amino-borane product. Addition of another 1 equiv of **B** to **4-Cy** accelerates this change, so that in less than 10 min at 298 K, **5-Cy** is the only observed organometallic species, alongside **C** and **B**. Under these latter conditions, where there is excess **B**, significant amounts of free **Z** are also observed by ^{11}B NMR spectroscopy, with subsequent dimerization of **Z** to **C**.

Scheme 6[a]



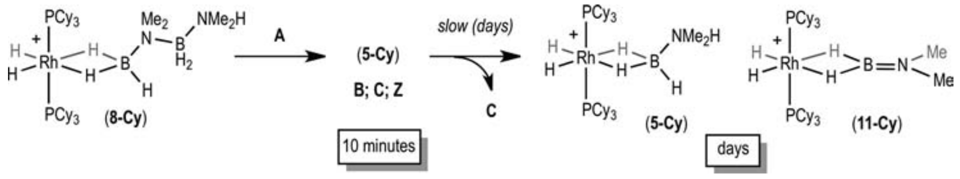
[a] [BAr$^F{}_4$]$^-$ anions are not shown.

The Rh(III) linear dimer complex [Rh(PCy$_3$)$_2$H$_2$(η^2-H$_3$B·NMe$_2$BH$_2$·NMe$_2$H)][BAr$^F{}_4$] (**8-Cy**) can be synthesized simply by addition of **B** to **10-Cy**. NMR data are in full accord with its formulation as a Rh(III) dihydride with an η^2-bound H$_3$B·NMe$_2$BH$_2$·NMe$_2$H, this being similar to the previously characterized **8-Bu**.[54] The analogous complex **8-Pr** has recently been characterized crystallographically,[73] as has a closely related H$_3$B·NMeHBH$_2$·NMeH$_2$ adduct.[57] With no excess **B** present, complex **8-Cy** is stable for days at 298 K. However, addition of a further 1 equiv of **B** rapidly (10 min) results in the appearance of **5-Cy**, **C**, and **Z**, which then evolves over 2 h to a mixture of **5-Cy**, **C** (70%), and **B** (30%) (Scheme 6). Addition of 1 equiv of **A** to **8-Cy** immediately results in the formation of **5-Cy** by displacement of **B**. A small amount of **C** and **Z** is also observed. This mixture then slowly evolves to give **C** and a mixture of **5-Cy**/**11-Cy** (Scheme 7).

These data indicate that in the early stages of catalysis (excess **A** and H$_2$), σ-bound complexes of **B** such as **8-Cy** [Rh(III)] or **4-Cy** [Rh(I)] will not be favored; rather those of **A** with rhodium in the 3+ oxidation state, i.e., Rh(III) **5-Cy**, will dominate. However, when they do form, as [**A**] is depleted, B−N bond cleavage of **B** (to form **A** and **Z**) occurs,[51,54] and this is accelerated by excess **B**. The formation of **5-Cy** and free **Z** as initial products of the reactions of bound **B** demonstrates this. Direct dehydrocyclization of bound **B** to **C** could also occur.[28] However, this would require catalysis by **A** or **B**, as we have no evidence for the Rh(I) complex **4-Cy** or the Rh(III) complex **8-Cy** undergoing dehydrocyclization to give **3-Cy** or **7-Cy**, respectively, when prepared in the absence of **A** or **B**. This is in contrast to TiCp$_2$-catalyzed systems that promote dehydrocyclization of **B** to form **C** directly,[28] but similar to studies on [Rh{P(C$_5$H$_9$)$_2$(PC$_5$H$_7$)}(η^2:η^1-H$_3$B·NMe$_2$BH$_2$·NMe$_2$H)][BAr$^F{}_4$] that show it is stable to further reaction, and only with excess **B** does it proceed to form **C**.[66] In the Rh(I) and Rh(III) systems described here, **B** is consumed (B−N bond cleavage and possibly dehydrocyclization) more slowly than the Rh(I) complex of **A** reacts, suggesting that consumption of **B** is slow during catalysis. A similar observation was made in the ^{i}Bu system.[54] All these observations point to **B** accumulating during the early stages of catalysis and then being consumed, as is observed. The slow reaction of **5-Cy** with **B** (days, Scheme 7) is in contrast to those of **5-Cy** with **A** (1 h, Scheme 4), **8-Cy** with **B** (minutes, Scheme 6), and **4-Cy** with **B** (minutes, Scheme 5). This suggests that the accelerating effects of additional amine borane are rather specific to **A** and **B** — potentially through complementary nonclassical B−H···H−N interactions.[82]

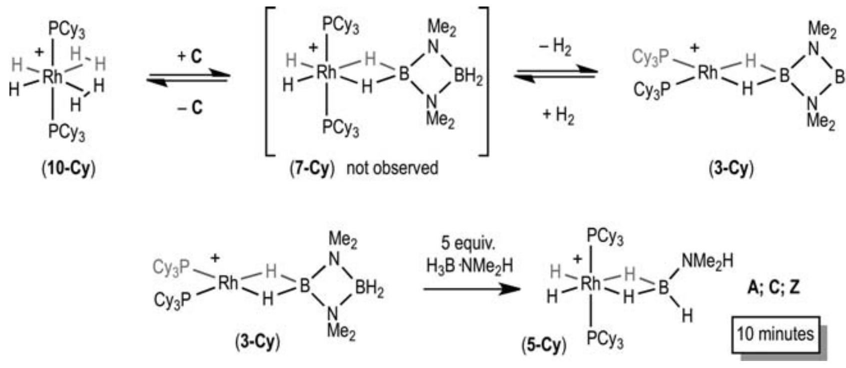
2.5. Reactivity with the Final Product, [H$_2$BNMe$_2$]$_2$. As the dimeric amino-borane **C** accumulates during catalysis, its reactivity with the Rh−phosphine fragments is potentially important. B−H σ-coordination complexes of **C** with Rh and Cr fragments have previously been reported.[24,53,54] Addition of **C** to **10-Cy** in a sealed NMR tube resulted in the immediate formation of the purple Rh(I) species [Rh(PCy$_3$)$_2$(η^2-[H$_2$BNMe$_2$]$_2$)][BAr$^F{}_4$] (**3-Cy**), by reductive elimination of H$_2$, in a 30:70 ratio with residual **10-Cy**/**C**. On addition of a further 5 equiv of **C**, this ratio changes to 90:10, indicating an equilibrium is established between the Rh(I) and Rh(III) species (Scheme 8). Dissolved H$_2$ (δ 4.6) is also observed. Presumably the reaction between **C** and **10-Cy** proceeds via Rh(III)-dihydride **7-Cy**, but steric pressure between the trans PCy$_3$ ligands and the cyclic amino-borane promotes rapid H$_2$ loss in this intermediate. Similar behavior has been proposed for the ^{i}Bu analogue, **7-Bu**.[54] Evidence for this transient Rh(III) dihydride complex of **C** comes from the ^{i}Pr analogue, **7-Pr**, in which H$_2$ loss is slightly less favorable and **7-Pr** can be isolated in the solid state, albeit only under an H$_2$ atmosphere. On addition of solvent, H$_2$ loss or amino-borane de-coordination is rapid.[53] **3-Cy** has been characterized by comparison with the reported NMR data for **3-Bu**,[54] and can also be made by direct addition of **C** to [Rh(PCy$_3$)$_2$L$_n$][BAr$^F{}_4$]. Addition of 5 equiv of **A** to **3-Cy** results in the formation of **5-Cy**. This proceeds by the displacement of **C** and rapid dehydrogenation of bound **A**, with **Z** observed during the early stages of the reaction (Scheme 8).

Scheme 7[a]



[a] [BAr$^F{}_4$]$^-$ anions are not shown.

Scheme 8[a]

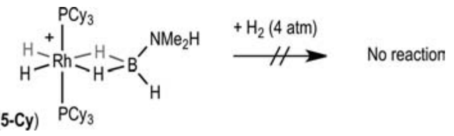


[a] $[BAr^F{}_4]^-$ anions are not shown.

These observations show that, under catalytic conditions, equilibrium coordination of **C** at a Rh(III) center can result in H_2 reductive elimination to form a reactive Rh(I) species. As **A** binds more strongly to Rh(III) than **C**, this switching in oxidation state will happen more frequently toward the end of catalysis, when the relative concentration of **C** is much higher than that of **A**.

2.6. Reactivity under a H_2 Atmosphere. Placing **5-Cy** under a H_2 atmosphere (4 atm) did not result in the displacement of **A** to form **10-Cy** (Scheme 9). This demonstrates that under sealed-tube conditions, it is unlikely that catalyst inhibition by H_2 will occur via the corresponding dihydrogen complex.

Scheme 9.



2.7. Qualitative Aspects of Catalysis: Effect of Added MeCN on the Rate of Dimerization of Amino-Borane. We have previously monitored the dehydrocoupling of **A** using both sealed NMR tube methods and those open to an argon atmosphere.[53,58] For the latter, quenching of solutions using a large excess of MeCN was used to stop the reaction at various time periods and allow for accurate ^{11}B monitoring of the boron-containing products. Catalysis in a sealed tube is considerably slower than in an open system, which we have suggested might be due to inhibition arising from H_2 buildup, by some yet to be determined process. We thus monitored the dehydrocoupling of **A** using the $[Rh(PCy_3)_2L_n][BAr^F{}_4]$ catalyst (0.072 M **A**, 5 mol %) in a system open to a slow flow of Ar, and quenched reaction aliquots using a large excess of MeCN. The resulting time/concentration plot is shown in Figure 1a. This shows **A** to decrease with time, **B** as an intermediate species, and **C** accumulating as the final product, with complete conversion after 2.8 h. This plot is very similar to that observed for P^iPr_3 and P^iBu_3 analogues, and gives a turnover frequency for the formation of **C** of ca. 7 h^{-1}, which is intermediate between those of the ^{i}Pr (4 h^{-1}) and ^{i}Bu (15 h^{-1}) catalysts under the same conditions of quenching and concentration.[53] No **Z** was observed under these conditions. We have recently reported that **Z** dimerizes to give the final product **C** by a second-order process at a rate that gives 50% conversion after 19 min (0.011 M initial concentration). If this process was operating here, a significant concentration of **Z** would be anticipated. Concerned that our sampling conditions might deplete **Z**, we tested quenching the reaction in an alternative manner: by diluting with difluorobenzene, rapid freezing, and then warming in the NMR probe.

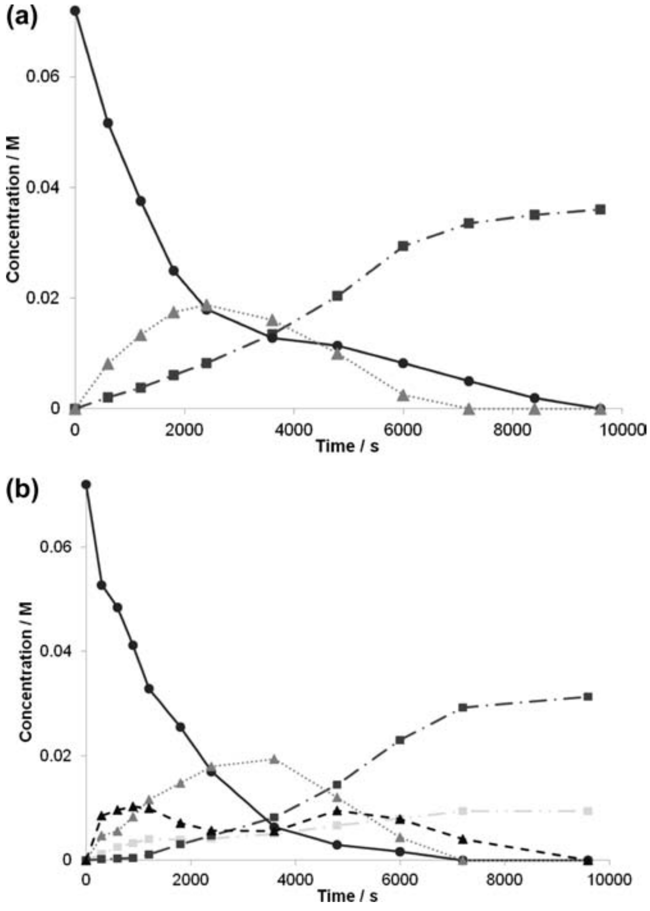


Figure 1. (a) MeCN-quenched catalysis and (b) non-MeCN-quenched catalysis with 5 mol % loading. Plot of ^{11}B concentration for the dehydrocoupling of $H_3B·NMe_2H$ (initial concentration = 0.072 M) using $\{Rh(PCy_3)_2\}^+$ generated in situ. Black circles, $H_3B·NMe_2H$ (**A**); gray triangles, $H_3B·NMe_2BH_2·NMe_2H$ (**B**); black squares, $[H_2BNMe_2]_2$ (**C**); gray squares, $HB(NMe_2)_2$; black triangles, $H_2B{=}NMe_2$ (**Z**).

Repeating the catalysis in a stirred, open system but now freezing aliquots revealed a profile that is more consistent with the actual reaction conditions, and demonstrates that MeCN plays a role in perturbing the observed relative concentrations of intermediates. Figure 1b shows the resulting time/concentration plot. This has similarities to the MeCN-quenched monitoring: **B** is an intermediate that reaches approximately the same maximum concentration of 0.02 M and is consumed by 7200 s, and conversion to **C** is complete after 10000 s. However, **Z** is now observed as an intermediate in appreciable concentrations (~0.01 M), and **C** grows in more slowly with an apparent induction period. It thus appears that a large excess of MeCN rapidly accelerates the dimerization of **Z** to give **C** so that, under MeCN quench conditions, **Z** is not observed. Similar acceleration has been noted by Paetzold in related cyclizations, in which *tert*-butylisonitrile is an effective catalyst for the cyclization of iminoboranes.[88]

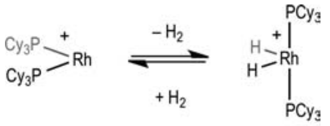
Also observed in the catalytic reaction mixture is the boranediamine $HB(NMe_2)_2$.[89] We have previously noted the formation of this species in sealed-tube experiments, as have others, but only at low concentrations.[21,24,26,28,54,58,65] $HB(NMe_2)_2$ has been shown to arise from addition of $NHMe_2$ to **Z**.[90] Given that under sealed tube conditions, or under MeCN quench, we see very little $HB(NMe_2)_2$, it is likely that this species arises from decomposition of the very reactive **Z** during sampling/analysis. For this reason we consider the absolute integrals of **Z** in these plots to be unreliable, and we discuss time/concentration profiles for **Z** in a qualitative rather than quantitative sense.

2.8. Qualitative Aspects of Catalysis: The Role of the Intermediate Linear Dimer $H_3B·NMe_2BH_2·NMe_2H$ B. Under the same conditions of concentration and sampling, $[Rh(PCy_3)_2L_n][BAr^F{}_4]$ (0.036 M **B**, 5 mol %) catalyzed the dehydrocoupling of **B** to ultimately form **C** (Supporting Information). **Z** and **A** are formed in appreciable concentrations at the early stages of catalysis, and these must arise from B−N bond cleavage. Complete conversion of **B** is observed after 7200 s. These data confirm that (i) **B** is an intermediate in the overall dehydrocoupling, (ii) B−N bond cleavage occurs under catalytic *and* stoichiometric conditions (vide supra), and (iii) consumption of **B** is slow, relative to that of **A**.

2.9. Qualitative Aspects of Catalysis: The Role of C. Having noted that coordination of **C** to a Rh(III) center promotes reductive elimination of H_2, thus establishing an equilibrium with Rh(I) species, and that the concentration of **C** builds during catalysis, it was of interest to see what influence additional (exogenous) **C** had on catalysis. Addition of 10 equiv of **C** to 0.072 M **A** containing 5 mol % $[Rh(PCy_3)_2L_n][BAr^F{}_4]$ had little impact on the rate of generation of **C** (7000 s, ToF 10 h^{-1}, Supporting Information). However, **A** is completely consumed after only 2100 s, compared to 7200 s in the absence of added **C** (cf. Figure 1). **B** is also observed. Addition of 10 equiv of **C** to a 0.036 M solution of **B** also had a marked impact on the profile of the reaction, with **B** falling rapidly and **C** produced faster, with full conversion of **B** at 3200 s (cf. 7000 s without added **C**). **Z** and **A** are also observed, arising from B−N bond cleavage (Supporting Information).

Additional **C** thus acts as a modifier to generate kinetically significant Rh(I) species (Scheme 10), and since **C** is the product of reaction, the effect is autocatalytic. On addition of **C**, the increase in the rate of consumption of **A** suggests that it is rapidly dehydrogenated by a Rh(I) species to give **Z**, although a slower Rh(III) cycle is still possible under the equilibrium conditions. Likewise, the consumption of **B** with excess **C** is significantly faster under Rh(I) conditions. This could occur by direct dehydrocylization of **B** to give **C** mediated by a Rh(I) species, as has been shown for Cp_2Ti systems,[18] and suggested for Ru[34] and heterogeneous Ni catalysts,[47] or it could also occur by B−N bond cleavage, vide supra.

Scheme 10[a]



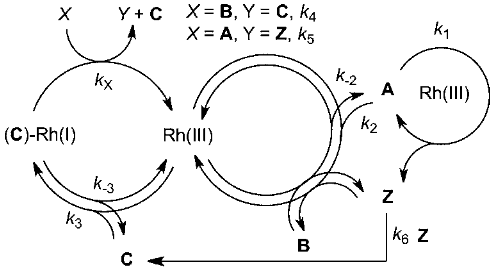
Addition of excess **C** probes Rh(I) by promoting reductive elimination of H_2

[a] $[BAr^F{}_4]^-$ anions not shown.

2.10. Qualitative Aspects of Catalysis: The Role of H_2 under Sealed-Tube Conditions. Performing the catalysis under standard conditions of concentration using **A** and **B** as substrates, but in a sealed NMR tube, resulted in very different profiles compared to open system conditions (Supporting Information). As a buildup of H_2 will force the system to rest at the Rh(III) organometallic products, these conditions probe this aspect of the catalytic cycle. Decay of **A** is now much slower, taking 15000 s to reach 50% conversion, compared with only 1200 s under open conditions. In addition, only small amounts of **Z** and **B** are now observed. When starting from **B**, catalysis is also much slower: just 35% conversion of **B** at 7500 s, compared with complete conversion in the same time under open conditions. Again, **Z** and **A** are observed as intermediates, arising from B−N bond cleavage. This slower catalysis is consistent with a Rh(III) cycle that slowly dehydrogenates **A** to **Z**, and also supports the conclusion that direct dehydrocyclization of **B** to **C** requires a Rh(I) species (i.e., **4-Cy**), rather than a Rh(III) (i.e., **8-Cy**). Complex **5-Cy** was the only organometallic species observed during catalysis under sealed tube conditions.

These stoichiometric and catalytic runs have revealed a rich and complicated reaction landscape for the dehydrogenation of **A** to ultimately give **C**. Given such complexity, we have chosen to concentrate on the major processes, while the subtleties and nuances of the system, albeit fascinating, are necessarily put to one side in this approach. In order to tie these observations together we turned to kinetic simulation of the catalyst systems.

2.11. Catalysis: Kinetic Simulations. In parallel with the stoichiometric and catalytic exploration of the Rh-catalyzed dehydrocoupling process, we engaged in iterative analyses of the reaction kinetics. These kinetic studies proved valuable not just in the support of the final model for the system, but more pivotally in the interrogation and dismissal of evolving mechanistic hypotheses and thus provision of feedback to the stoichiometric and catalytic investigations. Although full analytical rate equations can be derived for catalytic systems,[91] complex reaction networks, such as the one investigated herein, can be very challenging to simplify for application under limiting conditions. A more pragmatic approach is to test various mechanistic hypotheses via model systems that are explored in computationally based kinetics simulations.[92,93] This technique can be applied in a qualitative manner to evaluate the viability of a model in a general sense, with or without numerical tensioning against experimental data sets, or in a quantitative manner to determine absolute values for the rate constants associated with some or all of the steps in the cycle. A quantitative analysis requires a comprehensive model and is usually limited to simple systems, certainly less complex than those discussed herein. We thus aimed to develop a minimal holistic model that can qualitatively account for the macroscopic temporal evolution of the system when starting from five different initial conditions (Figures 2 and 3).[94]



$$\left[\, k_1 = \{(n\,(k_{RhCl}\text{-}k_{Rh+})) + (k_{Rh+}[Rh(III)]_0)\} \,\right]$$

Figure 2. Catalytic cycle employed to generate a qualitative predictive model for the kinetics of the catalyzed dehydrocoupling of **A** to **C**, via **Z** and **B**.

We began with three data sets experimentally obtained with $[\mathbf{A}]_0$ = 0.072, 0.12, and 0.15 M, all three employing 5 mol % Rh precatalyst. As discussed earlier, data for **Z** were unreliable due to further reactions during sampling, and thus while **Z** was included as a component in our models, we focused on obtaining reliable predictive profiles for the experimental temporal concentration data of **A**, **B**, and **C**. In our initial analysis we examined whether the profiles were consistent with catalysis predominantly proceeding via a simple **A**→**B**→**C** sequence, as was found for example in the Cp_2Ti-catalyzed system,[28] but augmented by partial conversion of **A** to **Z**, and the uncatalyzed dimerization of **Z** to give **C**.[51] The decay in **A** was found to be approximately first order in all three runs, with **B** growing and then decaying as would be expected. However, inconsistent with a simple **A**→**B**→**C** sequence was the profile for the decay of **B** and growth of **C** occurring after the peak in concentration of **B**. Instead of a simple decay process, there was the onset of a period of pronounced rate acceleration. Attempts to describe this behavior by inclusion of H_2 in the model and then controlled inhibition/acceleration of catalysis through solution-phase saturation/outgassing equilibria were not successful, primarily because of a concomitant effect on the

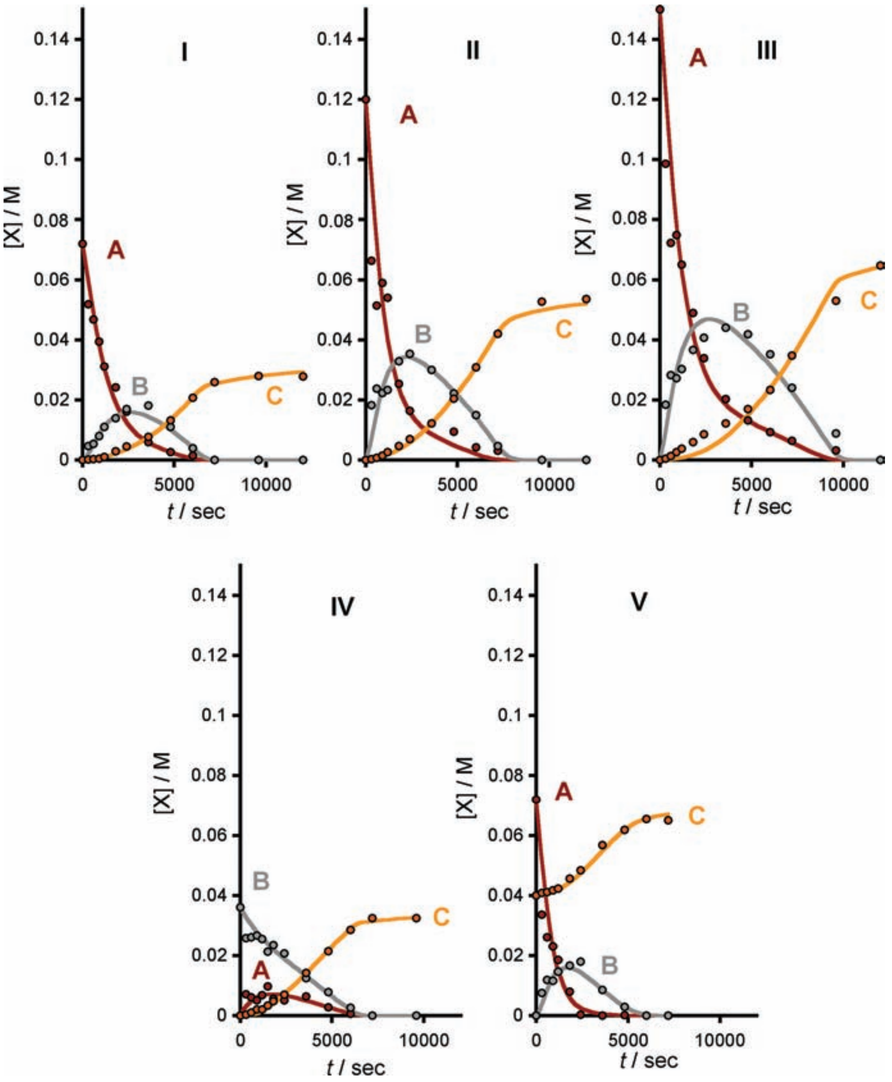


Figure 3. Temporal concentration profiles of five different starting conditions in the dehydrocoupling of **A** to **C**, via **B** and **Z**. Data points are experimentally determined concentrations. Solid lines are the profiles predicted by the qualitative model outlined in Figure 2.[95]

decay in **A**. A range of other inhibition/acceleration loops were also tested without success. A second approach lay in Rh-catalyzed equilibration of **A** with **Z** and **B**, and then accelerating the uncatalyzed dimerization of **Z** to **C** through a progressive change in reaction medium, e.g., polarity.[88] However, this did not account for the accelerated decay in **B**.

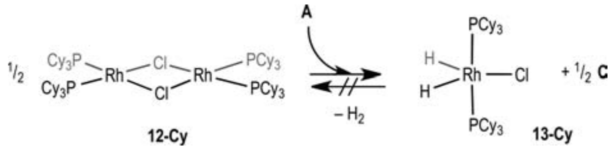
Ultimately, there were two key factors that led to the generation of a successful model (Figure 2). The first was the observation that the pseudo-first-order rate constants for decay in **A** were nearly identical for all three data sets: $6.6(\pm 0.3) \times 10^{-4}\ \mathrm{s}^{-1}$ over the first two half-lives. This was inconsistent with the change in $[\mathrm{Rh}]_0$, since this is more than doubled across the series, as is reflected in the proportional increases in the rate of generation of **B**. Moreover, additional runs at $[\mathbf{A}]_0 = 0.072$ with $[\mathrm{Rh}]_0 = 2.5$ and 7.5 mol % resulted in identical rates of conversion of **A**. Since there is no conversion of **A** in the absence of catalyst, this indicated that there were (at least) two types of catalyst being generated, with the concentration of one of these being independent of $[\mathrm{Rh}]_0$ and $[\mathbf{A}]_0$. The latter restriction suggested that the solvent, the only component that is constant between runs, contained a limiting quantity of a high-affinity modifier. Further work, vide infra, identified chloride ion as the most likely source of modified catalyst, and the final model thus includes a pseudo-first-order conversion of **A** to **Z** (k_1) arising from parallel catalysis (see inset to Figure 2). The unmodified cationic Rh(III) was also employed to turn over **A** + **Z** → **B** in a reversible telescoped multistage process (k_2). The second key factor was the generation of a mechanism for a mild autocatalytic influence of **C** occurring via a Rh(III)-to-Rh(I) switch (K_3). This then allowed rising rates for conversion of **B** to **C** (k_4) and for conversion of **A** to **Z** (k_5) in the later stages of catalysis when **C** begins to accumulate. Finally, the background uncatalyzed dimerization of **Z** (k_6) to **C** provides a pathway for initiation of the autocatalysis. This model, while complex, was then able to qualitatively account not just for catalysis at different initial concentrations of **A** (Figure 3, graphs I, II, and III) and the accelerating effect on turnover of **A** (k_5) when **C** is present from the start (graph V), but also for reactions starting with **B**, that generate **A** and **Z** (k_{-2}) and thus **C** (graph IV).

2.12. A Neutral Rh(III) Parallel Catalyst.

It is clear from the analysis of the reaction kinetics that there is a constant concentration of a very effective additional catalyst that turns **A** into **Z** under a pseudo-first-order process. The conditions used for catalysis involve generation of the active $[\mathrm{Rh(PCy_3)_2L}_n]$-$[\mathrm{BAr^F{}_4}]$ species in situ by halide abstraction using $\mathrm{Na[BAr^F{}_4]}$ to precipitate NaCl. We reasoned that low concentrations of chloride might be present in the difluorobenzene. Indeed, the dielectric constant of difluorobenzene is greater than those of both $\mathrm{CH_2Cl_2}$ and THF, but less than that of acetone, for which NaCl has measurable solubility, and so very low saturated concentrations of chloride might be expected.[96,97] If this were the case, then the initial starting material $[\mathrm{Rh(PCy_3)_2Cl}]_2$ (**12-Cy**) would be formed,[75] simply by recombination of chloride with $[\mathrm{Rh(PCy_3)_2L}_n][\mathrm{BAr^F{}_4}]$. The amount of this complex that is generated would be limited to the solubility of the chloride ion initially present, and would thus be low but constant between runs. If this were an excellent catalyst for the consumption of **A** then this could account for the observed rate of decay of **A**, acting as a parallel catalyst to the cationic systems described above.[98]

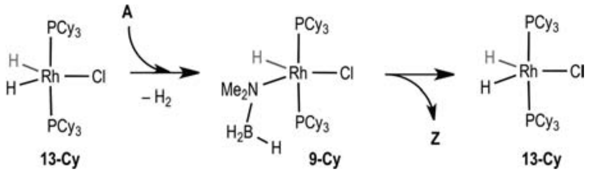
Addition of **A** [0.072 M] to 2 mol % (per Rh) of **12-Cy** in difluorobenzene solution in a sealed system resulted in an immediate reaction ($\mathrm{H_2}$ evolution), reaching 65% conversion to **C** after 7500 s, and demonstrating that **12-Cy** is indeed a competent precatalyst. This represents a $\mathrm{ToF_{50}}$ of 43 $\mathrm{h^{-1}}$, nearly two orders of magnitude faster than for the cationic system ($\mathrm{ToF_{50}} = 0.7\ \mathrm{h^{-1}}$, 5 mol %; $\mathrm{ToF_{50}}$ is the turnover frequency at 50% production of **C**). Both **Z** and **B** are observed as intermediates, but **B** is generated in much lower concentrations than in the cationic systems, and was not consumed over the monitored time period. Conversion of **A** does not proceed much past 65%. However, addition of more **A** restarts catalysis at approximately the same rate. Addition of **C** neither inhibits nor accelerates catalysis.[99] We suggest the (reversible) buildup of an inactive dimeric metal species at low [**A**] to account for this behavior (vide infra). Under stoichiometric conditions, addition of 2 equiv of **A** to **12-Cy** forms the Rh(III) species $\mathrm{Rh(PCy_3)_2H_2Cl}$ (**13-Cy**)[100] and **C**, quantitatively by NMR spectroscopy (Scheme 11). Small quantities of **B** were also observed. Given these observations, and that $\mathrm{H_2}$ loss from **13-Cy** has been shown to be slow at 373 K,[100] we suggest that the real catalyst under turnover conditions is the neutral Rh(III) dihydride complex, **13-Cy**. Consistent with this, in a sealed system (2 mol %) **13-Cy** is also a catalyst for the dehydrogenation of **A**, showing essentially the same rate as reactions catalyzed by **12-Cy**. The only organometallic species present during and at the end of catalysis is **13-Cy**. In an open system, catalysis is considerably faster: for **12-Cy**, $\mathrm{ToF_{50}} = 75\ \mathrm{h^{-1}}$ (0.5 mol %).[101] Although fast, these rates are still considerably slower than those reported for chelate−Rh(I) systems,[58] $(\eta^5\text{-}\mathrm{C_5H_3(SiMe_3)_2})_2\mathrm{Ti}$,[29] Ru−bifunctional PNP systems,[34] and some Rh(0) nanoparticle systems.[48] Nevertheless, the presence of even small amounts of such an efficient catalyst alongside the cationic system would result in the observed kinetic profiles. Further support for the involvement of the chloride species is provided by the addition of [PPN]Cl (PPN = bis-triphenylphosphineiminium) to a difluorobenzene solution of **10-Cy** that resulted in the clean formation of **13-Cy**. We suggest that as fluorobenzene and difluorobenzene are common solvents in the preparation of the ^{i}Pr[53] and ^{i}Bu[70] analogues from chloride precursors, it is possible that the chloride is carried over in these systems as well, although it might also be that the modifying effect of added chloride is rather system specific to $\mathrm{PCy_3}$.

Scheme 11



Although the full details of the mechanism of dehydrogenation of **A** by **13-Cy** remain to be resolved, we suggest that protonation of a metal hydride, followed by $\mathrm{H_2}$ loss, similar to that suggested for main-group and $\mathrm{d^0}$ catalyst systems,[19,22,102] is a plausible process. This would afford an amido-borane intermediate, **9-Cy**, that then rapidly undergoes β-elimination to re-form **13-Cy**, alongside $\mathrm{H_2}$ and **Z** (Scheme 12). In this process the metal stays in a constant oxidation state. This mechanism also accounts for faster turnover, as a lower barrier to the N−H activation step would be expected for a neutral system; this has been suggested to be the rate-limiting step in cationic systems.[51,54] Alternative mechanisms include halide-

Scheme 12. Mechanism Suggested for the Dehydrogenation of A Using $Rh(PCy_3)_2H_2Cl$



mediated intramolecular deprotonation of NH (and subsequent BH bond oxidative addition),[30] a σ-CAM mechanism[72] from a B–H σ-complex to give base-stabilized boryl (that then undergoes N–H activation), or a concerted B–H/N–H activation.[103] In a closed system **13-Cy** has not reacted appreciably with **B** after 1 h, in contrast to **A**, although after 16 h partial conversion to **C** is observed, showing that under the conditions of catalysis the dehydrogenation of **A** is essentially selective. Catalyst systems related to **12-Cy** (and by inference **13-Cy**) have been synthesized by Manners and co-workers, who reported that $Rh(PCy_2H)_3Cl$ is a competent catalyst for the dehydrogenation of **A** to give **C**. Pertinently, addition of the "phosphine sponge" $B(C_6F_5)_3$ accelerated catalysis, suggesting the formation of $Rh(PCy_2H)_2Cl$ as the active species.[39]

On the basis of DOSY experiments, complex **13-Cy** has been reformulated as a chloride-bridged dimer in toluene solution.[104] If such a dimer was itself inactive, but dissociates on addition of **A** to give an active momoneric species, this would account for the catalyst deactivation/reactivation on depletion/addition of **A**. The formation of a related dimeric species is a plausible explanation for the attenuation of activity of the system under sealed tube conditions, and suggests that the pressure of H_2 can affect the position of any equilibrium present. This is supported by previous observations by Werner[105] and Tolman[106] that the position of closely related dimer/monomer equilibria can be affected significantly by H_2 pressure. Studies are underway to put these ideas on a firmer mechanistic footing and will be reported in due course.

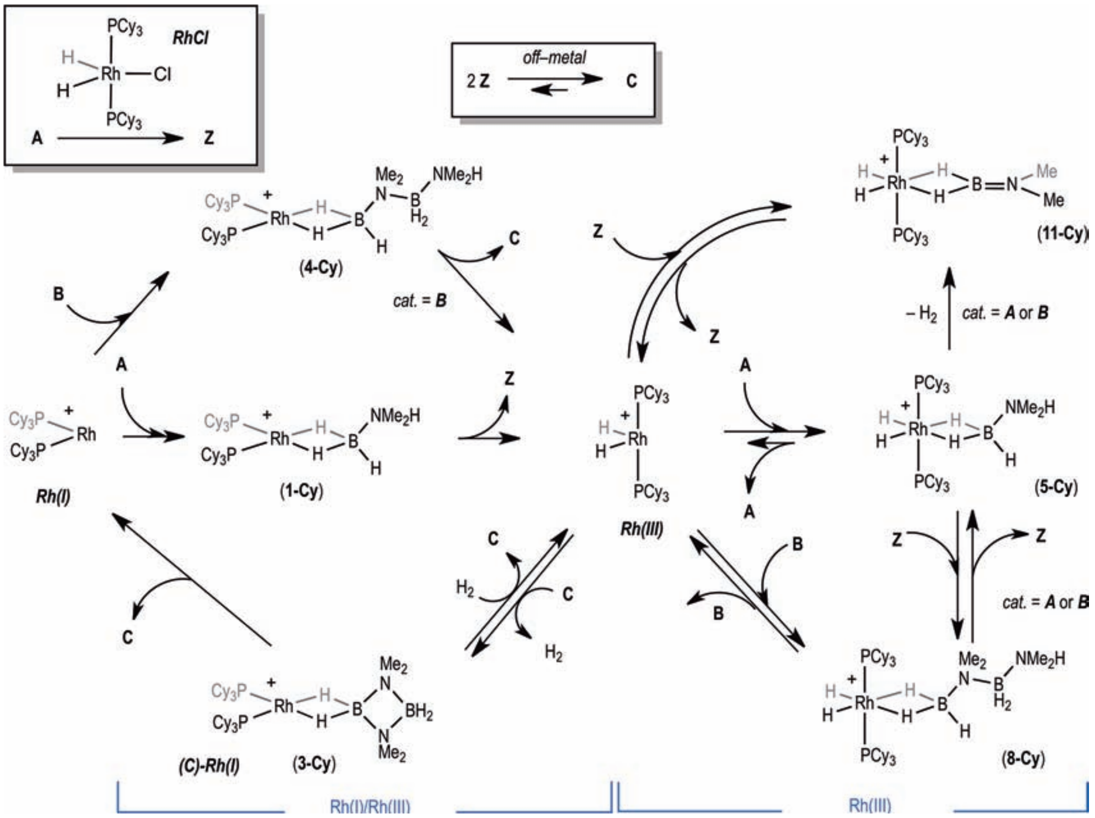
3. DISCUSSION

These combined stoichiometric, qualitative catalytic and kinetic simulation studies lead to a mechanism for the dehydrocoupling of $H_3B{\cdot}NMe_2H$ using the $[Rh(PCy_3)_2L_n][BAr^F{}_4]$ system as presented in Scheme 13.

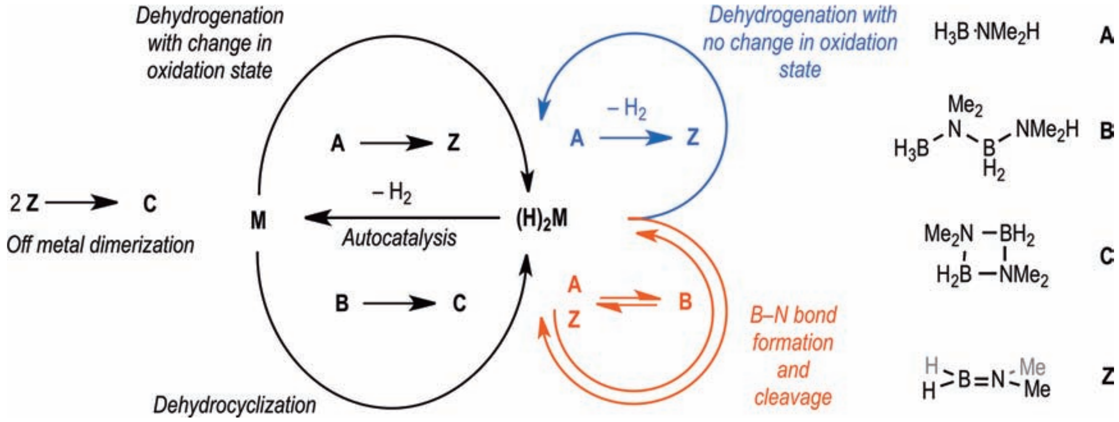
This is clearly a complex mechanism, with a number of competing equilibria. However, the following key points arise:

- Dehydrogenation of **A** to **Z** is fast with cationic Rh(I) catalysts, but slow with cationic Rh(III) catalysts.
- As H_2 loss from the $\{Rh(PCy_3)_2H_2\}^+$ fragment is slow in these cationic systems, this is the resting state during catalysis, consistent with previous experimental observations. Whether amine-borane coordinates to this fragment (e.g., **5-Cy** or **8-Cy**), or the amino-borane coordinates (**11-Cy**), will depend on the relative concentrations of the relevant boron species at any one time.
- The linear dimer, **B**, is formed on a Rh(III) species. B–N bond cleavage to return **A** and **Z** is also mediated at a Rh(III) center. Depending on the relative concentrations of **A**, **Z**, and **B**, the reaction can proceed in either

Scheme 13. Relationships between Species Observed in Stoichiometric and Catalytic Reactions, Underpinned by Kinetic Simulations



Scheme 14. General Scheme for Dehydrocoupling of $H_3B{\cdot}NMe_2H$ Using Transition Metal Catalysts



- direction as there is no net H_2 loss. This is consistent with calculations that show the process to be close to thermoneutral ($\Delta G = -2.3$ kcalmol^{-1}).[34]
- Dehydrocyclization of **B** is likely mediated by a Rh(I) center.
- **C** is a modifier in catalysis and acts in an autocatalytic role to move the system between the slow Rh(III) regime and the fast Rh(I) regime.
- There is a parallel neutral catalyst based upon $Rh(PCy_3)_2H_2Cl$ in constant but low concentration that efficiently dehydrogenates **A** to give **Z**.
- Dimerization of **Z** to give **C** occurs "off-metal", and can be accelerated by MeCN.
- Complementary BH···HN interactions are likely to play a role in lowering barriers to many of these processes, although they have not been explicitly modeled here.

These observations lead to a simplified, and broadly applicable, mechanistic scheme for the dehydrocoupling of $H_3B{\cdot}NMe_2H$, as shown in Scheme 14. This builds substantially upon previous observations regarding the mechanism.[7,9,28,44,51,62] Aspects of this scheme can be applied to many transition-metal and main-group systems that catalyze the dehydrocoupling of **A** to give **C**, and below we present selected literature examples to demonstrate this.[107]

For the exceptionally fast [Rh(chelating bis-phosphine)]$^{58+}$ catalyst systems, the formation of **Z**, by dehydrogenation of **A** with a change in oxidation state at Rh, followed by loss of H_2, has been implicated. These catalysts contrast with the cationic monodentate phosphine systems, inasmuch as the intermediate Rh(III)-dihydride rapidly loses H_2 to re-form a Rh(I) species in the chelate systems, whereas this is slow (in the absence of modifier **C**) in the monodentate phosphine systems. Rhenium(I) phosphine catalysts are also suggested to undergo a change in oxidation state,[33] as are photogenerated group 6 and 7 carbonyl systems[24,38] and $TiCp_2$-based catalysts.[28,29] Constant oxidation state cycles can be fast or slow for the dehydrogenation of **A**, and we suggest that this is due to the relative barriers to N−H activation. These are likely to be lowered in neutral systems, as compared to cationic, and "inner-sphere" cationic Rh(III)[51,54,66] and Ir(III)[43,51] systems are also likely operate by this route. Outer-sphere ligand-assisted, Noyori-like processes in which the metal oxidation state does not alter also fit into this category.[34,61,62,64] Interestingly, these latter species are generally very fast catalysts. Main-group catalysts also work at constant oxidation state, and some have been shown to operate via an intermediate similar to **B**, resulting from combination of **A** and **Z**, via an N−H activation pathway. Cyclization of this intermediate (not by H_2 loss, but by H-transfer) forms **C** and regenerates the active catalyst.[19,20] The recently reported Ni(0)−amido complexes[42] may also work via a similar mechanism, although a change in oxidation state cannot be discounted.

The formation of the linear intermediate diborazane **B** occurs from the combination of "monomer" units **A** and **Z**, as is suggested for Ru,[24,34] Rh,[40] Ir,[51] and Ti[28] systems, although in the latter system this is suggested to occur via combination of **A** with a N−H-activated intermediate. Generation of **B** is also related to the coordination/insertion oligomerization mechanism for the catalyzed formation of B−N oligomeric and polymeric species from primary amine-boranes.[18,50,57] Consumption of **B** can occur by dehydrocyclization to give **C**, as shown convincingly for $TiCp_2$ systems.[28] Alternatively, B−N bond cleavage can occur in **B** to regenerate the simple monomers **A** and **Z**.[34,51,62] Analogous redistribution reactions of linear diborazanes, related to **B**, have recently been reported to be catalyzed by iridium−pincer complexes.[50] Where **B** is definitively shown not to be an intermediate, for example with photogenerated $CpFe(CO)_n$,[31] the simple dehydrogenation of **A** to give **Z** is suggested. Finally, **Z** dimerizes to give **C** by a bimolecular "off-metal" process, as has been demonstrated using a latent source of **Z**,[51] and will always occur when there is free **Z** present. As far as we are aware, the mild autocatalysis induced by product **C** has not been previously reported.

4. CONCLUSIONS

The dehydrocoupling of amine-boranes catalyzed by transition metals is a complex process whose mechanism is very dependent on the metal and the amine-borane substrate. Even by focusing on the apparently simple process of $[Rh(PCy_3)_2]^+$-catalyzed dehydrogenation of $H_3B{\cdot}NMe_2H$ to the cyclic amino-borane $[H_2BNMe_2]_2$, we reveal here a remarkable diversity in mechanism. The study has elucidated a number of key processes: dehydrogenation by catalytic cycles that can involve a change in oxidation state at Rh, or have a constant oxidation; autocatalysis; parallel catalysis; B−N bond cleavage; and dehydrocyclization. Although this leads to a rather elaborate mechanism, it does allow for an overall mechanistic scenario that we propose to be broadly applicable to many other reported catalysts for the dehydrogenation of $H_3B{\cdot}NMe_2H$; some aspects may also be relevant to Rh catalysis for other amine-borane systems. We also suggest the involvement of nonclassical BH···HN hydrogen bonds in these processes, as highlighted recently by others[37,83−85] in non-metal-promoted processes. It will be of significant interest to see if such favorable interactions can be definitely shown to occur in transition-metal-based systems, and studies are underway in our laboratories to probe this.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full synthetic and characterization data for the new complexes reported; stoichiometric reactions and time/concentration plots of catalysis; details of the kinetic simulations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(98) Adventitious fluoride, or hydroxide, potentially could act in the same way. However, as we pretreat the difluorobenzene by stirring over alumina (to remove fluoride), then CaH_2 (to remove water), and finally distilling under vacuum, we suspect the levels of F^- or H_2O would be low and also not reproducible. Although fluoride can be generated from addition of strong nucleophiles, such as cyanide, to fluoroaromatics [see: Sun, H.; DiMagno, S. G. *J. Am. Chem. Soc.* **2005**, *127*, 2050], it is unlikely this is occurring here. We see no evidence for C−F activation of the fluoro-aromatic in these systems [see, for example: Panetier, J. A.; Macgregor, S. A.; Whittlesey, M. K. *Angew. Chem., Int. Ed.* **2011**, *50*, 2783] that might also generate a fluoride on the metal. Such reactivity would also be inconsistent with our kinetic model. Trace chloride thus appears to be the most reasonable candidate.
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NOTE ADDED IN PROOF

Highly organized metal templated transition states that involve hydrogen−bonding of additional substrate, related to the BH···HN interactions implied in this paper, have recently been suggested to occur in intermolecular styrene hydroamination. See: Brinkmann, C.; Barrett, A. G. M.; Hill, M. S.; Procopiou, P. A. *J. Am. Chem. Soc.* **2012**, in the press. DOI: 10.1021/ja209135t.