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Dehydrocoupling of Dimethylamine Borane Catalyzed by $Rh(PCy_3)_2H_2Cl$

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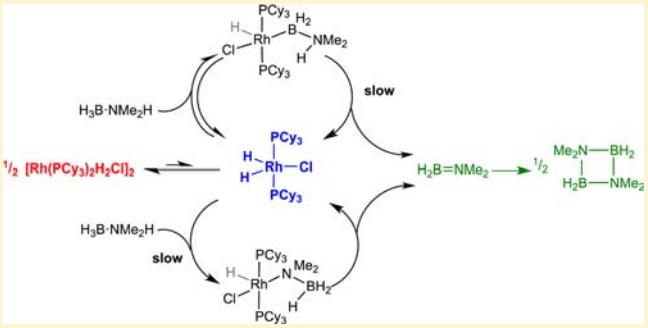
Supporting Information

ABSTRACT: The Rh(III) species $Rh(PCy_3)_2H_2Cl$ is an effective catalyst (2 mol %, 298 K) for the dehydrogenation of $H_3B{\cdot}NMe_2H$ (0.072 M in 1,2-$F_2C_6H_4$ solvent) to ultimately afford the dimeric aminoborane $[H_2BNMe_2]_2$. Mechanistic studies on the early stages in the consumption of $H_3B{\cdot}NMe_2H$, using initial rate and H/D exchange experiments, indicate possible dehydrogenation mechanisms that invoke turnover-limiting N−H activation, which either precedes or follows B−H activation, to form $H_2B{=}NMe_2$, which then dimerizes to give $[H_2BNMe_2]_2$. An additional detail is that the active catalyst $Rh(PCy_3)_2H_2Cl$ is in rapid equilibrium with an inactive dimeric species, $[Rh(PCy_3)H_2Cl]_2$. The reaction of $Rh(PCy_3)_2H_2Cl$ with $[Rh(PCy_3)H_2(H_2)_2][BAr^F{}_4]$ forms the halide-bridged adduct $[Rh(PCy_3)_2H_2(\mu\text{-}Cl)H_2(PCy_3)_2Rh][BAr^F{}_4]$ (Ar^F = 3,5-$(CF_3)_2C_6H_3$), which has been crystallographically characterized. This dinuclear cation dissociates on addition of $H_3B{\cdot}NMe_2H$ to re-form $Rh(PCy_3)_2H_2Cl$ and generate $[Rh(PCy_3)_2H_2(\eta^2\text{-}H_3B{\cdot}NMe_2H)][BAr^F{}_4]$. The fate of the catalyst at low catalyst loadings (0.5 mol %) is also addressed, with the formation of an inactive borohydride species, $Rh(PCy_3)_2H_2(\eta^2\text{-}H_2BH_2)$, observed. On addition of $H_3B{\cdot}NMe_2H$ to $Ir(PCy_3)_2H_2Cl$, the Ir congener $Ir(PCy_3)_2H_2(\eta^2\text{-}H_2BH_2)$ is formed, with concomitant generation of the salt $[H_2B(NMe_2H)_2]Cl$.



INTRODUCTION

The dehydrocoupling of amine boranes, $H_3B{\cdot}NR_2H$ or $H_3B{\cdot}NRH_2$ (R = alkyl), as catalyzed by transition-, alkaline-earth-, and main-group-metal−ligand complexes, has attracted considerable recent interest.[1−5] This is due to the potential for control over H_2 release kinetics necessary for chemical hydrogen storage applications, for which the parent amine borane, $H_3B{\cdot}NH_3$, has a high concentration (wt %) of hydrogen,[6−9] or the formation via dehydropolymerization of $H_3B{\cdot}NRH_2$ of novel B−N polymeric materials that are isoelectronic with polyolefins.[10−12] Mechanistic studies probing dehydrogenation and subsequent coupling for $H_3B{\cdot}NH_3$ generally rely on the observation of non-metal-containing boron intermediates or final products, although there are reports that comment in detail on the specific role of the metal.[13−18] For the primary amine boranes $H_3B{\cdot}NRH_2$ final products can be polyaminoboranes, arising from dehydropolymerization, or borazines. Recent advances have demonstrated the isolation of metal-bound aminoboranes[18−22] and oligomerization products[23] or the observation of hydrogen redistribution (transfer hydrogenation) reactions between aminoboranes and amine boranes.[24−26] For the secondary amine borane $H_3B{\cdot}NMe_2H$, **A** (Scheme 1a), there is nominally a single final product, $[H_2BNMe_2]_2$, **C**, this being formed via an initial dehydrogenation of **A** and then dimerization of the resulting aminoborane $H_2B{=}NMe_2$, **Z**. This apparent simplicity has allowed for deeper insight into both the boron products formed during dehydrocoupling and the role of the metal catalyst.[27−32] In addition to $H_2B{=}NMe_2$, the linear dimer $H_3B{\cdot}NMe_2BH_2{\cdot}NMe_2H$, **B**, has also been observed as an intermediate in some systems.[4,27,28,33−35] Complex **B** can arise from direct coupling of two **A**'s, as has been shown for Ti(II)-based systems,[10] although recent results suggest the active catalyst is Ti(III),[36] or from coupling of **A** and **Z** at a metal center.[28,29] For the transition-metal catalysts, inner-sphere activation via σ-B−H−M interactions[37] is implicit and N−H activation is involved in the rate-limiting step in many cases. Outer-sphere dehydrogenation mechanisms have been proposed to operate in a manner related to alcohol oxidation using bifunctional catalysts;[14,15,38] while d^0 metal catalyst systems (groups 2 and 13) show complementary, but different,

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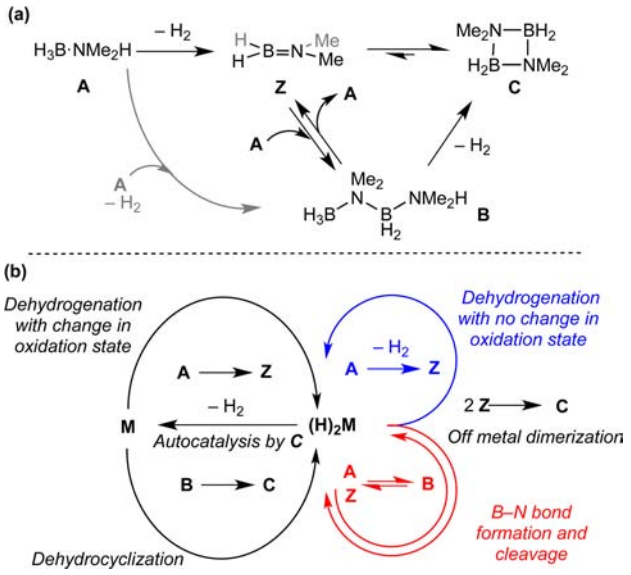
Scheme 1. (a) Observed Intermediates and Final Product C in the Dehydrocoupling of A Using Transition-Metal Catalysts[27−29] and (b) General Scheme for Dehydrocoupling of A Based upon Studies Using the $\{Rh(PCy_3)_2\}^+$ System[33]

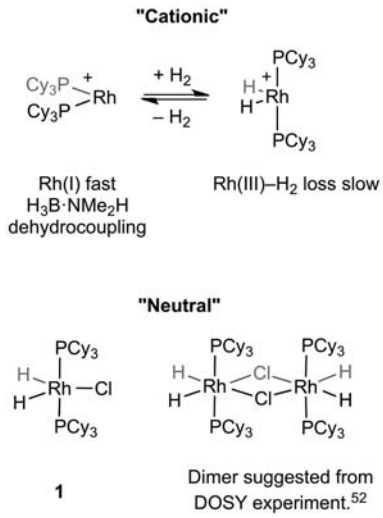


mechanisms.[39−41] Systems that involve multimetallic activation of amine boranes have also been reported.[42,43]

We have recently reported on the use of a variety of $\{M(L_2)\}^+$ fragments [M = Rh, Ir; L_2 = $(PR_3)_2$ or chelating phosphine] to probe the dehydrocoupling of **A** or $H_3B{\cdot}NMeH_2$.[23,29,34,35,44−48] Using $[Rh(PCy_3)_2][BAr^F{}_4]$ as a precatalyst [Ar^F = 3,5-$C_6H_3(CF_3)_2$], we were able to propose a detailed mechanistic model, supported and informed by kinetic simulations, that demonstrates a complex and nuanced mechanistic landscape in which the cationic rhodium catalyst shuttles between a fast Rh(I)/Rh(III) regime and a slower constant oxidation state rhodium(III) dihydride regime, Scheme 1b.[33] In particular, this mechanism invokes **C** as a modifier in catalysis, in which it acts in an autocatalytic role moving the system between the slow rhodium(III) dihydride regime and the fast Rh(I) regime by promoting reductive elimination of H_2. Simulations, verified by experiment, also suggested the presence of an additional parallel catalyst in low, but invariant, concentrations that promoted the pseudo-first-order consumption of **A**. On the basis of preliminary experiments, we suggested a plausible formulation for this additional catalyst was neutral $Rh(PCy_3)_2H_2Cl$,[49] **1** (Scheme 2). This would form from rapid hydrogenation of $[Rh(PCy_3)_2Cl]_2$,[50,51] which itself is likely formed via traces of chloride that could be in low but saturated concentrations in the solvent. Neutral complex **1** operates relatively rapidly to dehydrogenate **A** to form aminoborane **Z**, which then can either enter the "cationic" cycle or simply dimerize to form final product **C**. Pertinently, Duckett and co-workers have suggested on the basis of NMR diffusion measurements (DOSY) that **1** is in fact a chloride-bridged dimer in solution, similar to $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2H_2$.[52] Interestingly, the structure of closely related $Rh(P^iPr_3)_2H_2Cl$ shows it to be a monomer in the solid state,[53] although this does not rule against a dimeric formulation in solution.

In this Article we explore the mechanism by which **1** dehydrogenates **A** and also comment on the likely species present in catalysis when **1** is combined with an excess of a cationic $\{Rh(PCy_3)_2H_2\}^+$ fragment, i.e., under the conditions found in cationic catalysis. We find the mode of consumption of **A** is consistent with the constant oxidation state Rh(III) portion of the overall scheme for dehydrocoupling (Scheme 1). Aspects of this work have been briefly discussed in introducing **1** as a plausible catalyst in the cationic dehydrogenation system.[33]

Scheme 2. Neutral and Cationic Catalysts for Dehydrocoupling of $H_3B{\cdot}NMe_2H$ Using $\{Rh(PCy_3)_2H_2\}^+$ Fragments



RESULTS AND DISCUSSION

Reactivity Studies on $Rh(PCy_3)_2H_2Cl$. Before describing the role of **1** in catalysis directly, we first discuss its likely form in the cationic system where $\{Rh(PCy_3)_2H_2\}^+$ is present in excess (5 mol % total catalyst loading, 0.072 M substrate). In this system the observed resting state is reported to be the Rh(III) σ-amine borane complex $[Rh(PCy_3)_2H_2(\eta^2\text{-}H_3B{\cdot}NMe_2H)]^+$, **2**, as shown by $^{31}P\{^1H\}$ NMR spectroscopy.[33] Under these conditions of catalyst concentration, a detection limit of ca. 10% of the total catalyst concentration is not unreasonable by $^{31}P\{^1H\}$ NMR spectroscopy, providing a threshold for detection of ca. 0.5 mol % and above for any other species present. Combination of equal amounts of **1** with $[Rh(PCy_3)_2H_2(H_2)_2][BAr^F{}_4]$,[54] as a source of the $\{Rh(PCy_3)_2H_2\}^+$ fragment, immediately forms the new chloride-bridged complex $[Rh(PCy_3)_2H_2(\mu\text{-}Cl)H_2(PCy_3)_2Rh][BAr^F{}_4]$, **3**, which was characterized by NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS),[55] and single-crystal X-ray diffraction (Scheme 3). The solid-state structure of **3**, Figure 1, exhibits a Rh−Cl−Rh core, in which the chloride sits on a special position in the unit cell, resulting in half of the molecule being generated by crystallographically imposed symmetry. In solution at room temperature (298 K, CD_2Cl_2) broad signals are observed in the ^1H and $^{31}P\{^1H\}$ NMR spectra for **3**, in particular a broad environment at δ −24.2 in the hydride region of the ^1H NMR spectrum and a single broad environment at δ 49.6 in the $^{31}P\{^1H\}$ NMR spectrum. Cooling to 200 K resolved these broad signals so that three separate, but very similar, species were observed in both the $^{31}P\{^1H\}$ and the ^1H NMR spectra, at individual chemical shifts that correspond well with the weighted-average room temperature chemical shifts, suggesting rapid interconversion among the three at 298

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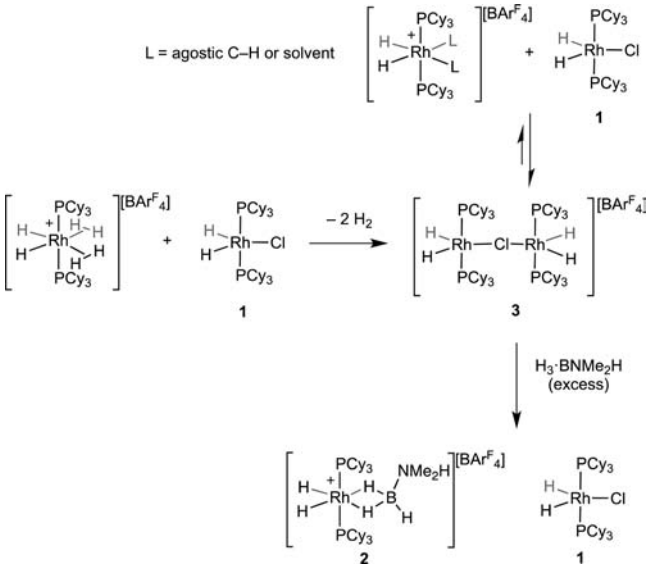
Scheme 3. Synthesis and Reactivity of 3



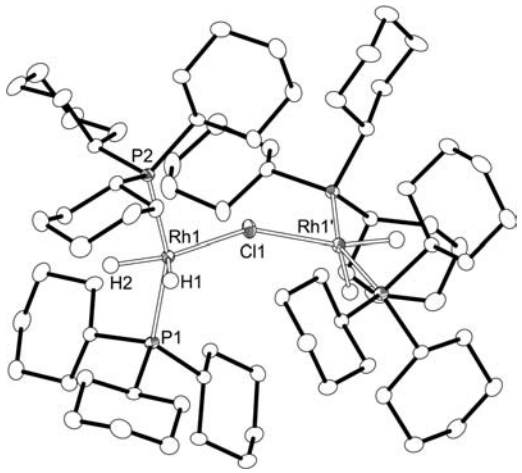


Figure 1. Solid-state structure of complex **3**. The $[BAr^F_4]^-$ anion and most hydrogen atoms are omitted for clarity. Displacement ellipsoids are shown at the 30% probability level. The crystallographically equivalent atoms are generated by the operation $-x, y, -z + {}^1/_2$. Selected bond distances (Å) and angles (deg): Rh1–P1, 2.3258(8); Rh1–P2, 2.3295(7); Rh1–H1, 1.51(3); Rh1–H2, 1.51(3); Rh1–Cl1, 2.4813(3); Rh1–Rh1′, 4.831(8); P1–Rh1–P2, 156.75(3); Rh1–Cl1–Rh1′, 153.61(5).

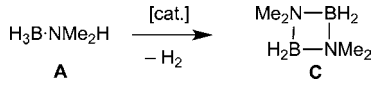
K (Figure S-1, Supporting Information), viz., δ 49.7 [d, J(RhP) = 115 Hz, ~10%], 47.5 [d, J(RhP) = 114 Hz, ~10%], 46.1 [d, J(RhP) = 113 Hz, 80%]. We assign these three species to an equilibrium mixture of **3** and the dissociated monomers, neutral **1** and cationic $[Rh(PCy_3)_2H_2L_2][BAr^F_4]$[54] (L = CH_2Cl_2 or agostic interaction), in a ratio of 8:1:1, respectively, at 200 K. The $^{31}P\{^1H\}$ and ^1H NMR spectra of independently prepared $[Rh(PCy_3)_2H_2L_2][BAr^F_4]$ at 200 K support this assignment, i.e., δ 47.5 [d, J(RhP) = 110 Hz]. The observation of a single ^{31}P and ^1H (hydride) environment for **3** at 200 K suggests a shallow potential energy profile for small changes in the Rh–Cl–Rh angle that allows for the equivalence of the hydrides and phosphorus environments.

Although complex **3** would likely form when **1** is in the presence of an excess of a latent source of $\{Rh(PCy_3)_2H_2\}^+$, under the additional constraint of excess $H_3B{\cdot}NMe_2H$ (i.e., during catalysis), it rapidly (time of mixing) reacts to return **1** and **2** (Scheme 3). At the end of catalysis, at low $[H_3B{\cdot}NMe_2H]$, **3** might also re-form (vide infra). Complex **3** is also broken up in the presence of $H_3B{\cdot}NMe_3$ and $H_3B{\cdot}NMe_2BH_2{\cdot}NMe_2H$ (**B**) to form **1** and the corresponding amine borane adducts $[Rh(PCy_3)_2H_2(\eta^2\text{-}H_3B{\cdot}NMe_3)][BAr^F_4]$ and $[Rh(PCy_3)_2H_2(\eta^2\text{-}H_3B{\cdot}NMe_2BH_2{\cdot}NMe_2H)][BAr^F_4]$, respectively.[33]

Complex **1** undergoes H/D exchange with D_2 to afford $Rh(PCy_3)D_2Cl$, as previously reported by James.[49] Presumably this occurs via a monomeric (or monobridged dimer) σ-bound intermediate, $Rh(PCy_3)_2H_2(D_2)Cl$, that then undergoes a σ-CAM (CAM = complex-assisted metathesis) exchange process.[56,57] Related to this, Duckett has reported that the monometallic pyridine adduct reversibly forms on addition of pyridine to **1**,[52] demonstrating reversible coordination of a Lewis base.

Catalysis. Using our standard open conditions under a slow flow of Ar, i.e., not in a sealed NMR tube (298 K, 0.072 M **A**, 2 mol % **1**, 1,2-$F_2C_6H_4$ solvent), complex **1** efficiently promotes the dehydrogenation of **A** to ultimately afford the cyclic aminoborane $[H_2BNMe_2]_2$, **C** (Scheme 4). The reaction

Scheme 4. Dehydrocoupling of $H_3B{\cdot}NMe_2H$, A



essentially goes to completion (i.e., ToN = 48), taking 1.7 h to reach 95% conversion. This can be compared to the $Rh(PHCy_2)_3Cl$ catalyst, reported by Manners and co-workers, that in the presence of $B(C_6F_5)_3$ (to remove one phosphine) mediates complete conversion of **A** to **C** in 10 h at 1 mol %.[58] A time–concentration profile for **1** as the catalyst is shown in Figure 2a. A significant concentration of the aminoborane $H_2B{=}NMe_2$, **Z**, is observed, which dimerizes to form **C**. The second-order rate constant for this process has been determined in various solvents, in which a metal fragment is not implicated in the dimerization.[26,29,33] Although the overall kinetics for catalysis are complex, the consumption of **A** follows pseudo-first-order kinetics, $k = (1.03 \pm 0.05) \times 10^{-3}$ s^{-1} (Figure 2b). This behavior is consistent with the cationic catalyst system at 5 mol % (0.072 M **A**) with a parallel catalyst in low concentration (0.5 mol % or less), which also shows a pseudo-first-order decay of **A**, and for which kinetic modeling suggests a pseudo-first-order rate constant similar to that determined here: $(0.58 \pm 0.01) \times 10^{-3}$ s^{-1}.[33] Under open conditions but at 1 mol % (i.e., an effective 0.5 mol % concentration of **1**), complex **3** also catalyzes the dehydrogenation of **A** (Figure S-4, Supporting Information) and also follows a pseudo-first-order profile with a rate constant $k = (0.37 \pm 0.01) \times 10^{-3}$ s^{-1}, again broadly consistent with that measured in the cationic system.

Under sealed NMR tube conditions (298 K, 0.072 M **A**, 2 mol % **1**, 1,2-$F_2C_6H_4$ solvent), complex **1** is a competent catalyst for the dehydrogenation of **A** to ultimately afford **C**. In contrast to the open system, this reaction does not go to completion, with only 70% conversion observed (i.e., ToN = 35). A time–concentration profile for this reaction is shown in Figure S-5 (Supporting Information). Although complete conversion to **C** is not observed, addition of more **A** to the catalyst system (by opening the NMR tube to Ar, addition of

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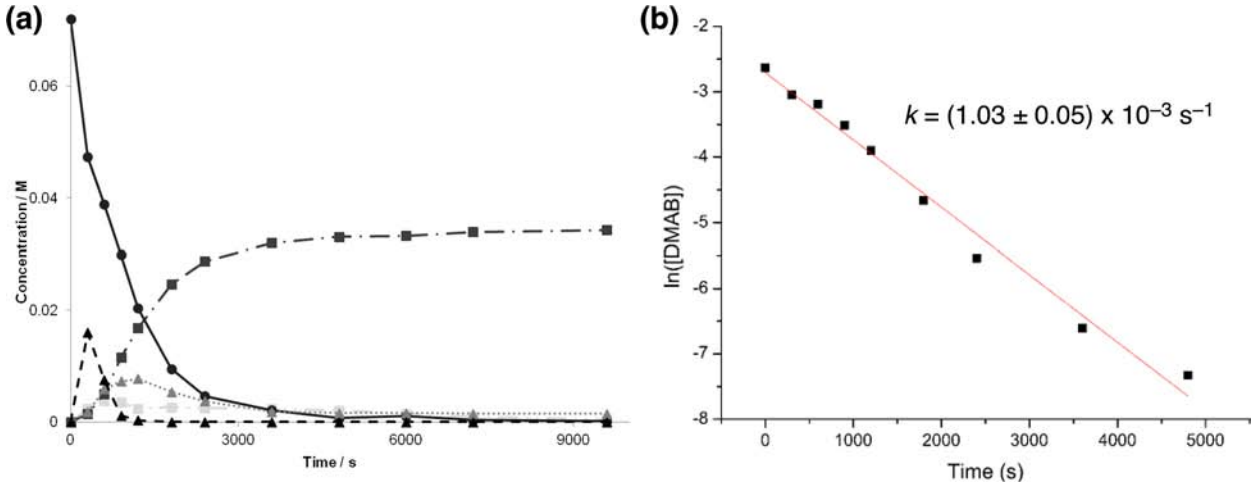

Figure 2. (a) ^{11}B concentration over time for the dehydrocoupling of $H_3B{\cdot}NMe_2H$ (initial concentration 0.072 M) using $Rh(PCy_3)_2H_2Cl$ (0.1 mL samples diluted with 0.25 mL of 1,2-$C_6H_4F_2$ under argon). (b) First-order plot of consumption of $H_3B{\cdot}NMe_2H$. Key: black circles, $H_3B{\cdot}NMe_2H$, **A**; black triangles, $H_2B{=}NMe_2$, **Z**; gray triangles, $H_3B{\cdot}NMe_2BH_2{\cdot}NMe_2H$, **B**; black squares, $[H_2BNMe_2]_2$, **C**; gray squares, $HB(NMe_2)_2$ (trace).

Table 1. Initial Rates for the Dehydrocoupling of $H_3B{\cdot}NMe_2H$, A, Using $Rh(PCy_3)_2H_2Cl$ in a Sealed System (High-Pressure NMR Tube, 298 K, 1,2-$F_2C_6H_4$ Solvent) at Given Initial Concentrations of A[a]

entry	[Rh] (M)	[$H_3B{\cdot}NMe_2H$] (M)	[$D_3B{\cdot}NMe_2H$] (M)	[$H_3B{\cdot}NMe_2D$] (M)	[$D_3B{\cdot}NMe_2D$] (M)	initial rate (10^{-5} M s^{-1})
1	0.00144	0.072				13.8 ± 0.4
2	0.00144	0.036				5.5 ± 0.4
3	0.00144	0.144				26.6 ± 0.4
4	0.00072	0.072				9.9 ± 0.4
5	0.00288	0.072				19.5 ± 0.4
6	0.00144		0.072			11.5 ± 0.4
7	0.00144			0.072		2.6 ± 0.4
8	0.00144				0.072	2.7 ± 0.4
9	0.00114	0.072[b]				14.0 ± 0.4

[a]Catalysis does not run to completion under these conditions; see the text. [b]A 25-fold excess of **C** was added.

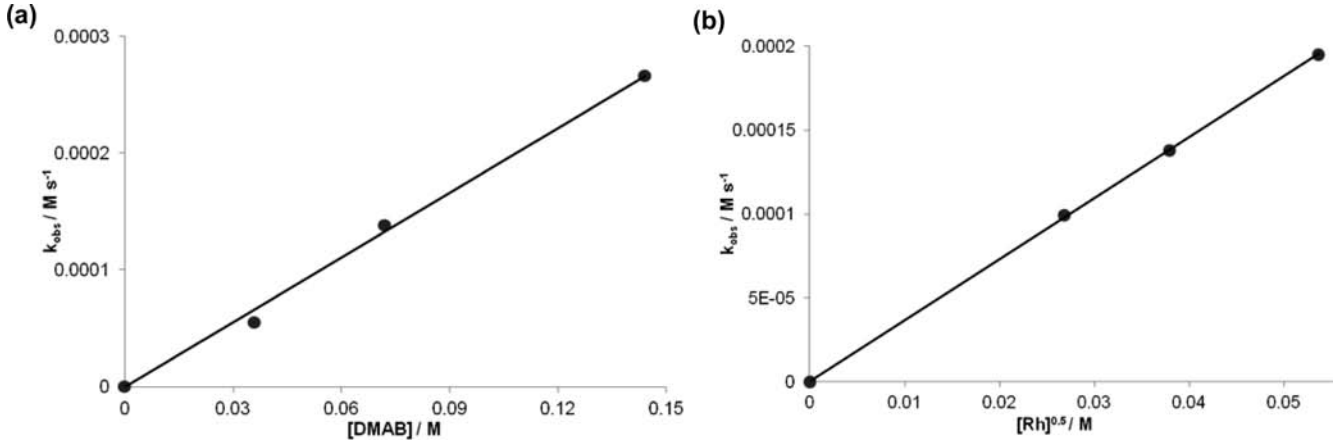

Figure 3. Initial rate versus concentration for (a) [DMAB] and (b) $[Rh(PCy_3)_2H_2Cl]^{1/2}$.

more **A**, and then resealing) gives essentially the same conversion (70%) and a very similar reaction profile (Figure S-6, Supporting Information). This demonstrates the catalyst remains active and does not decompose significantly. We assign this incomplete conversion under sealed conditions to inhibition by H_2 formed from the dehydrocoupling, as no inhibition is observed in the open system. Interestingly, under these sealed tube conditions, we see very little of the linear dimer intermediate **B**, unlike in the cationic system,[35] although **Z** is still observed in appreciable concentrations.

Given the relative complexity of the overall system and the significant challenge in modeling the holistic temporal evolution of the starting materials, intermediates, and final products, we chose to study the mechanism for dehydrogenation of **A** using the method of initial rates,[59] combined with isotopic labeling, to determine the order of the reaction and the rate-limiting processes.

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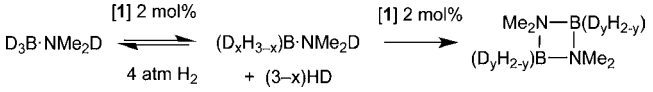
Initial Rate and Labeling Experiments. Table 1 shows the results of initial rate experiments conducted under sealed NMR tube conditions (298 K, **1**, 1,2-$F_2C_6H_4$ solvent). These data were fitted to the approximately linear region of **A** consumption over the first 180 s of catalysis.

Entries 1−3 demonstrate a first-order dependence on [**A**], and Figure 3a shows this relationship graphically. Entries 1, 4, and 5 (Figure 3b) show that the initial rate is linearly dependent on $[Rh(PCy_3)_2H_2Cl]^{1/2}$, which is characteristic of a fast monomer−dimer equilibrium being present during catalysis, in which the dimer is dominant but sits off the cycle and the monomer is the active species.[60] This inference is consistent with Duckett's assignment of **1** as a dimer.[52] Such an order dependence and dimer−monomer equilibria have previously been noted in Pd-catalyzed alkene arylations,[61] hydrolysis of methylparathion,[62] and Heck couplings.[63] Likewise, transfer hydrogenation processes using Shvo's catalyst,[64,65] including amine borane dehydrogenation,[14] also invoke such a kinetic regime. Monomer−dimer equilibria have also been suggested for cyclohexene hydrogenation by $[Rh(PR_3)_2Cl]_2$[66] and Rh-catalyzed hydroboration.[67] We see no evidence for the formation of mixed-valence dimers, such as $[Rh(PR_3)_2H_2(\mu\text{-}Cl)_2Rh(PR_3)_2]$ (R = Phephos, *p*-tolyl), which are in equilibrium with the corresponding rhodium(I) chloride-bridged dimers by loss of H_2.[66,68,69] Indeed, extended exposure of **1** to a vacuum did not remove H_2, consistent with previous reports.[70] By contrast to **1**, a first-order dependence on the catalyst has been measured in the dehydrogenation of $H_3B{\cdot}NMeH_2$ using $Ir(^tBuPOCOP^tBu)H_2$ [$^tBuPOCOP^tBu$ = κ^3-1,3-$(OP^tBu_2)_2C_6H_3$], consistent with a monomeric catalyst.[12] There was no change in the initial rate when an excess (25-fold) of **C** was added in addition to **A** [$(14.0 \pm 0.4) \times 10^{-5}$ M s^{-1}, cf. entry 1]. This rules out an autocatalytic role for the final product, in contrast to the cationic system.[33]

Isotopic labeling experiments give further insight into the likely mechanism of dehydrogenation. Entry 7 shows a substantial primary kinetic isotope effect (KIE) (k_H/k_D = 5.3 ± 1.2) for N−H/N−D activation when using $H_3B{\cdot}NMe_2D$, indicating that irreversible N−H transfer is likely to be involved in the rate-limiting process. A similar KIE has been noted for amine borane dehydrocoupling using $TiCp_2$ systems.[27] When using $D_3B{\cdot}NMe_2H$, a much smaller (presumably secondary and/or equilibrium, vide infra) KIE is observed (k_H/k_D = 1.2 ± 0.1), entry 6, suggesting that B−H cleavage is not involved in the rate-limiting process. Consistent with this conclusion, double-labeled $D_3B{\cdot}NMe_2D$ afforded a k_H/k_D of 5.1 ± 1.2, entry 8, identical within experimental error to that observed with $H_3B{\cdot}NMe_2D$. Under a H_2 atmosphere (ca. 4 atm) with $H_3B{\cdot}NMe_2H$ as the substrate, the initial rate did not change appreciably compared to standard sealed tube conditions, and the reaction also ran to 70% conversion under these conditions (ToN = 35). We suggest that this reflects the low solubility of H_2 in 1,2-$F_2C_6H_4$,[71] meaning that hydrogen only modifies the catalytic cycle at low $[H_3B{\cdot}NMe_2H]$ near the end of catalysis, possibly by competitively forming a σ-H_2 complex with one of the intermediates. H_2 has been shown to reversibly bind to $Ir(PR_3)_2H_2Cl$ (R = Cy, ^iPr) to give the corresponding dihydrogen adducts.[72,73] To our knowledge, the Rh congeners have not been reported. We find no evidence of reaction between **1** and H_2 (4 atm, 1,2-$F_2C_6H_4$ solution) by ^1H NMR spectroscopy: no chemical shift change or broadening of the sharp hydride resonance at δ −22.9 is observed under these conditions. We thus suggest that H_2 coordinates to an intermediate resulting from B−H activation (vide infra; see **D**, Scheme 6), attenuating the rate-limiting N−H activation that is proposed to occur via β-hydrogen transfer to a vacant site on the metal. Under all these conditions of catalysis (open and sealed) we did not observe an induction period, the solutions retained their homogeneous appearance through the course of catalysis, and the rate of catalysis was not significantly affected by the addition of Hg(0). These observations point toward a homogeneous rather than a heterogeneous process,[74,75] although caution should always be exercised in definitively ruling out a heterogeneous process.[76]

Having established that a dimer−monomer equilibrium operates in catalysis, and N−H activation is involved in the turnover-limiting step, H/D exchange experiments allowed for further insight into the mechanism, and in particular for probing of the relative order of N−H and B−H activation. Treatment of $Rh(PCy_3)_2D_2Cl$ with $H_3B{\cdot}NMe_3$ (which has no NH and therefore does not undergo dehydrogenation) resulted in no H/D exchange at the Rh−H or B−D sites, in contrast to other related, cationic systems.[23,35] In these examples exchange is suggested to occur via a B−H/Rh−H σ-CAM[56,57] process that generates a base-stabilized boryl (see Scheme 6) which then can re-form the σ-complex with scrambling of H and D. Such base-stabilized boryls are also invoked in the hydroboration of alkenes by $H_3B{\cdot}NMe_3$ as catalyzed by a $\{Rh(PR_3)_2\}^+$ fragment.[77] In contrast, when $D_3B{\cdot}NMe_2D$ was subjected to catalysis using **1** (2 mol %) but under 4 atm of H_2, this resulted in rapid H/D exchange at boron in the amine borane starting material as measured by ^{11}B NMR spectroscopy (Figure S-8, Supporting Information) *but not at N*, to the detection limits of ^1H NMR spectroscopy, with the concomitant formation of the final product $[(D/H)_2BNMe_2]_2$ and $HD_{(diss)}$ (Scheme 5). This indicates that B−H coordination

Scheme 5



and activation at the metal center is fast and reversible compared to irreversible dehydrogenation, consistent with the small isotope effect for B−D cleavage, vide supra. A similar scenario has been reported for the dehydrogenation of $H_3B{\cdot}NMe_2H$ using $\{(\eta^5\text{-}C_5Me_4H)_2Ti\}_2N_2$ as the catalyst in which B−H activation is proposed to precede rate-limiting N−H activation.[30] Base-stabilized boryls have also been suggested to form in Ir systems on reaction with $H_3B{\cdot}NH_3$.[78] We suggest that it is steric factors that suppress B−H activation of $H_3B{\cdot}NMe_3$ with **1**, although we cannot discount the possibility that the inability to form N−H···Cl−Rh secondary interactions when using $H_3B{\cdot}NMe_3$ might raise the barrier to B−H activation by removing a lower energy pathway for approach of the amine borane to the metal. Related interactions have been proposed for the dehydrogenation of $H_3B{\cdot}NH_3$ by ruthenium bis(trimethylsilyl)amino catalysts.[21] Treatment of $Rh(PCy_3)_2H_2Cl$ with $Et_3B{\cdot}NMe_2H$,[79] which would probe N−H activation only, due to the lack to B−H, also resulted in no reaction. It is possible that this lack of reaction is also due to increased steric demand compared to that of **A**.

Suggested Catalytic Cycle. On the basis of these observations, we suggest the mechanism for the *initial* dehydrogenation of **A** by **1** is as outlined in Scheme 6. Dimeric

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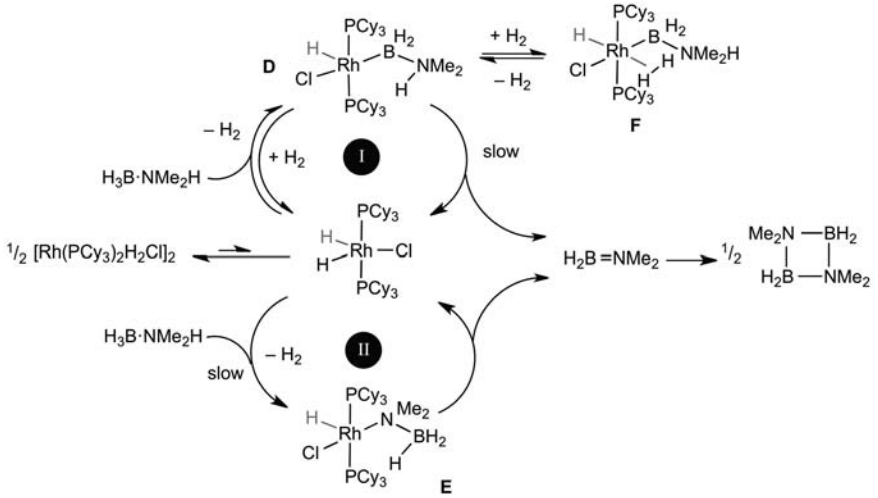
Scheme 6. Proposed Mechanisms for the Dehydrogenation of $H_3B{\cdot}NMe_2H$, A, Using $Rh(PCy_3)_2H_2Cl$, 1, To Ultimately Form the Cyclic Dimer $[H_2BNMe_2]_2$, C, via Dimerization of Z, As Determined by Monitoring the Early Phase of Catalysis[a]



[a]See the text for a discussion of the role of the minor intermediate **B**.

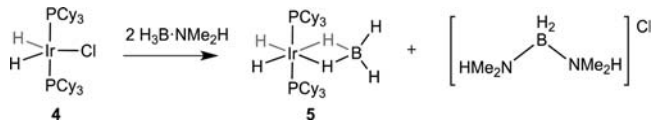
1, sitting off cycle, is in rapid equilibrium with the corresponding monomer. This can then undergo reversible B–H activation (cycle I) or irreversible N–H activation (cycle II). Cycle I presumably proceeds via an initial σ-CAM process, similar to that postulated for H/D exchange in **1**,[56] as both B–H oxidative addition to form a Rh(V) species and H_2 loss from **1**[70] to form a Rh(I) species are likely disfavored. The resulting base-stabilized boryl (intermediate **D**) then proceeds in an irreversible N–H β-H transfer to eliminate $H_2B{=}NMe_2$, **Z**, and regenerate the active catalyst. Cycle I captures the significant KIE associated with NH/ND, while the small KIE associated with BH/BD is presumably due to an equilibrium isotope effect. Cycle II proceeds via irreversible N–H activation (protonation) to give an aminoborane intermediate, **E**, possibly with a supporting B-agostic interaction.[36,80] The small KIE associated with BH/BD might be due to a secondary isotope effect or B–H activation becoming synchronous with N–H activation. The collected data do not allow for the discrimination between these two pathways, I or II. However, the rapid H/D exchange observed in the substrate **A** must invoke an intermediate (**F**) that is closely related to **D** on cycle I.

This proposed mechanism is similar to that suggested for cationic catalyst systems of Rh and Ir, in which the oxidation state of the metal does not change.[29,35] It also has similarities to those reported for Ti,[27,30] Cr,[81] and Mn[82] catalysts and aspects of the mechanism proposed for alkaline-earth metals.[40] This cycle differs from those that invoke concerted B–H/N–H activation pathways, which have correspondingly more leveled B–H and N–H k_H/k_D values than reported here.[14,15] The products of both B–H activation[45] and N–H activation[36,80] of amine boranes have been isolated. Turculet and co-workers have recently reported calculations that suggest a stepwise N–H, followed by a higher energy B–H, activation in the dehydrogenation of $H_3B{\cdot}NH_3$ (Cy-PSiP)Ru(N(SiMe$_3$)$_2$) [Cy-PSiP = κ^3-(2-R$_2$PC$_6$H$_4$)$_2$SiMe], although here N–H activation is calculated to occur via an intramolecular deprotonation mechanism and subsequent elimination of HN(SiMe$_3$)$_2$[21] and is somewhat related to that calculated for ammonia borane dehydrogenation using Ni(NHC)$_2$ systems (NHC = *N*-heterocyclic carbene).[16,83,84]

Although our studies probe the very early stages of the reaction, as Figure 2a shows, a small but significant amount of $H_3B{\cdot}NMe_2BH_2{\cdot}NMe_2H$, **B**, is also formed as an intermediate and then consumed. Formation of **B** might occur via a metal-mediated combination of **A** and **Z**,[28,29] or from two molecules of **A** with concomitant release of H_2.[27] Consumption of **B** likewise could re-form **A** and **Z**,[28,33] or proceed by intramolecular dehydrocylization.[27,33]

Deactivation at Low Catalyst Loadings. The studies reported above were conducted using 2 mol % catalyst loadings. On moving to a lower catalyst loading of 0.5 mol % for **1** in an open system (298 K, 0.072 M **A**, 1,2-F$_2$C$_6$H$_4$ solvent), we found that irreversible catalyst deactivation occurred, resulting in only 60% consumption of **A**, with a profile that did not fit a simple kinetic model. Addition of more **A** did not restart catalysis to any significant level. This deactivation is in sharp contrast to catalysis using **3** at the same effective loadings, which has the counterpart $\{Rh(PCy_3)_2H_2\}^+$ fragment coordinated with **1** and returns 100% conversion of **A** to **C** at 0.5 mol % loadings at a rate similar to that of the cationic system at 5 mol % (vide supra). We thus suggest that this cationic fragment acts to stabilize the more active $Rh(PCy_3)_2H_2Cl$ against decomposition by some as yet undetermined mechanism. Using the Ir congener to **1**, $Ir(PCy_3)_2H_2Cl$, **4**, in catalysis gave insight into likely decomposition products. In contrast to complex **1**, complex **4** does not turnover to dehydrogenate **A**. Instead, under catalytic conditions (**4**, 20 mol %, 298 K, 1,2-F$_2$C$_6$H$_4$ solvent) a slow (50000 s) consumption of only *2 equiv* of amine borane is observed. The final product is not **C**, but instead the salt $[H_2B(NMe_2H)_2]Cl$ is formed (as identified by NMR spectroscopy[85,86]). The organometallic partner to this is the borohydride complex $Ir(PCy_3)_2H_2(\eta^2\text{-}H_2BH_2)$, **5**, Scheme 7, giving mass balance to this process (see the Supporting

Scheme 7. Reaction of 4 with $H_3B{\cdot}NMe_2H$



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Information for full details). Complex **5** can be independently synthesized by addition of $Na[BH_4]$ to **4** and analogous way to $Ir(P^tBu_3)_2H_2(\eta^2\text{-}H_2BH_2)$[87] and is essentially inactive for the dehydrogenation of **A**. The equivalent Rh complex which we suggest might also form at low loadings of **1**, $Rh(PCy_3)_2H_2(\eta^2\text{-}H_2BH_2)$, **6**,[51] is also inactive. Consistent with this, **6** is observed to form as the significant species (95%, $^{31}P\{^1H\}$ NMR spectroscopy) under open conditions (**1**, 0.5 mol %, 60% conversion of **A**, 16 h). Heinekey and co-workers has reported a catalytically dormant product in amine borane dehydrogenation catalysis using the $Ir(^tBuPOCOP^tBu)H_2$ catalyst that invokes a borohydride-like structure, although it is better formulated as a σ-BH_3 complex of the parent dihydride.[88] Interestingly, Manners and co-workers have reported that $Ir(PHCy_2)_2Cl$ does catalyze the dehydrogenation of **A**, while no $[H_2B(NMe_2H)_2][Cl]$ is reported to be formed.[58] Clearly, these subtle changes in the phosphine compared to **4** influence the course of this catalysis.

CONCLUSIONS

We have shown here that $Rh(PCy_3)_2H_2Cl$, **1**, is an effective catalyst for the dehydrogenation of $H_3B{\cdot}NMe_2H$, confirming our initial suggestion that it is a cocatalyst present in low, but constant, concentration in the cationic $\{Rh(PCy_3)_2H_2\}^+$ system.[33] Mechanistic studies based upon initial rates and isotope-labeling experiments indicate that catalysis proceeds by turnover-limiting N−H activation, which precedes or follows B−H activation, to form $H_2B{=}NMe_2$, which then dimerizes to give $[H_2BNMe_2]_2$. This model for consumption of $H_3B{\cdot}NMe_2H$ sits well with the constant oxidation state Rh(III) portion of the overall scheme for dehydrocoupling (Scheme 1b). An additional detail is that the active catalyst is in rapid equilibrium with an off-cycle dimeric species, $[Rh(PCy_3)_2H_2Cl]_2$.

Compound **1** is also related to the pincer-type catalyst $Ir(^tBuPOCOP^tBu)H_2$, in that they are both ML_2X_3 systems, and the latter has been shown to dehydrocouple $H_3B{\cdot}NH_3$[89] and $H_3B{\cdot}NMeH_2$[11,12] to give oligomeric and polymeric BN-containing products, which is calculated to occur via a concerted N−H/B−H activation mechanism for $H_3B{\cdot}NH_3$.[90] In contrast, $H_3B{\cdot}NMe_2H$ is only dehydrogenated slowly.[12] Whether this reflects simply the increased steric demands of the pincer ligand or an increased barrier to the intrinsic N−H/B−H activation at the metal center is currently not defined. In this context it will be interesting to explore if **1** will also dehydrogenate $H_3B{\cdot}NMeH_2$ and whether polyaminoboranes are formed.

ASSOCIATED CONTENT

Supporting Information

Full experimental details for complexes **3**, **5**, and **6**, variable-temperature NMR data for **3**, X-ray characterization of **3**, **5**, and **6**, details of mechanistic studies, and CIF data for $\mathbf{3}.2C_6H_5F$. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 915250, **3**) and can be obtained via www. ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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