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Zirconium-Catalyzed Amine Borane Dehydrocoupling and Transfer Hydrogenation

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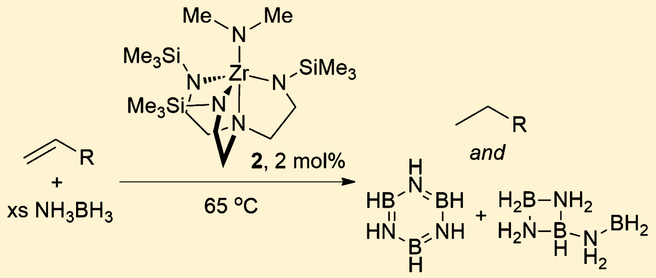
S *Supporting Information*

ABSTRACT: κ^5-$(Me_3SiNCH_2CH_2)_2N$-$(CH_2CH_2NSiMe_2CH_2)Zr$ (**1**) has been found to dehydrocouple amine borane substrates, $RR'NHBH_3$ (R = R′ = Me; R = ^{t}Bu, R′ = H; R = R′ = H), at low to moderate catalyst loadings (0.5−5 mol %) and good to excellent conversions, forming mainly borazine and borazane products. Other zirconium catalysts, $(N_3N)ZrX$ [(N_3N) = $N(CH_2CH_2NSiMe_2CH_2)_3$, X = NMe_2 (**2**), Cl (**3**), and O^tBu (**4**)], were found to exhibit comparable activities to that of **1**. Compound **1** reacts with Me_2NHBH_3 to give $(N_3N)Zr(NMe_2BH_3)$ (**5**), which was structurally characterized and features an η^2 B−H σ-bond amido borane ligand. Because **5** is unstable with respect to borane loss to form **2**, rather than β-hydrogen elimination, and **2**−**4** do not exhibit X ligand loss during catalysis, dehydrogenation is hypothesized to proceed *via* an outer-sphere-type mechanism. This proposal is supported by the catalytic hydrogenation of alkenes by **2** using amine boranes as the sacrificial source of hydrogen.



INTRODUCTION

Application of amine boranes in materials science, for hydrogen storage, and in organic synthesis demonstrates the usefulness of these simple Lewis acid−base adducts as materials precursors and chemical reagents.[1−5] The most pointed driver for recent study of amine borane dehydrogenation has been the potential use of these molecules for hydrogen storage, owing to their high hydrogen content by weight and relative ease of hydrogen loss. However, thermal degradation of amine boranes is poorly controlled and time-consuming.[3,6] Thus, catalysts that operate under desirable conditions (i.e., mild temperatures and faster reaction times) to form products in a controlled manner have been sought. Some of the most active catalysts that have been reported are capable of operating at ambient temperatures using rare and expensive group 9 transition metals such as iridium and rhodium.[7−10] This is a highly active field of study, and catalysts from across the periodic table have been reported including transition-metal and main group compounds.[11−19]

Group 4 catalysts were some of the earliest studied for amine borane dehydrocoupling and have elicited interest from several groups due to their high reactivity and mechanistic richness. Manners,[20−22] Chirik,[23] Rosenthal,[24] Wass,[25,26] Beweries,[24,27] and Baker[28] have all presented detailed studies of related group 4 metallocene complexes. These independent studies indicate that titanium compounds demonstrate greater activity than their heavier congeners and that increased electron donation and steric pressure from ancillary ligands decrease reactivity. Substrate selectivity was also observed for group 4 metallocenes, which demonstrated high activity for secondary amine borane dehydrocoupling, while these compounds were almost inert toward ammonia borane. The lower activity of these metallocene compounds with NH_3BH_3 is perhaps due to competing formation of stable amido borane complexes that precipitate out of solution.[29] Efforts to circumnavigate this issue include the use of bulkier and well-defined 14 e^- zirconocene precursors that enhance solubility. However, the dehydrocoupling activity of these compounds with ammonia borane was still lower in comparison to the secondary amine borane Me_2NHBH_3.[23] Interestingly, nonmetallocene group 4 complexes such as $M(NMe_2)_4$ (M = Ti, Zr) were equally active toward secondary and primary amine boranes.[24]

The mechanism of dehydrocoupling is remarkably varied among group 4 metals despite the similarities in the complexes that have been reported. Chirik and Manners both proposed B−H bond activation either through oxidative addition to form a boryl complex or through a transient three-center two-electron interaction.[20,21,23] Additionally, Chirik and Manners each observed formation of the amino borane $Me_2N{=}BH_2$, which is consistent with β-hydride elimination. However, Manners primarily observed the formation of the linear diborazane, $Me_2NHBH_2Me_2NBH_3$, consistent with a coupling process.

As amine borane dehydrocoupling advances, an emerging application for this catalysis is as a sacrificial hydrogen source for hydrogenation reactions.[7,30−37] The commercial importance of hydrogenation is indisputable, but safety concerns over the use of gaseous hydrogen remain. Group 4 metals have been rarely used in hydrogenation catalysis[21,38] despite their high

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abundance and low cost. Presumably the propensity of group 4 catalysts to undergo β-hydride elimination has stymied further advances.[39] The triamidoamine-supported zirconium complex κ^5-$(Me_3SiNCH_2CH_2)_2N(CH_2CH_2NSiMe_2CH_2)Zr$ (**1**) is generally resistant to β-hydrogen elimination[40] and is active for catalytic heterofunctionalization reactions.[41−43]

Investigation of amine borane dehydrocoupling by **1** led to the exploration of other related triamidoamine zirconium compounds $(N_3N)ZrR$ ($(N_3N) = N(CH_2CH_2NSiMe_2CH_2)_3$; R = NMe_2 (**2**), Cl (**3**), and O^tBu (**4**)), which appear to proceed via an outer-sphere-type mechanism. This observation has been capitalized in the hydrogenation of unsaturated organic substrates using these zirconium catalysts and amine boranes as a hydrogen source.

■ RESULTS AND DISCUSSION

Amine Borane Dehydrocoupling. Initial dehydrocoupling efforts were focused on sampling the catalytic activity of **1** toward a variety of amine borane substrates ($RR'NHBH_3$, R = R′ = Me; R = R′ = H; R = ^tBu, R′ = H). Upon mixing solutions of **1** with amine borane substrates in deuterated solvent (benzene-d_6 or THF-d_8) at ambient temperature, a small amount of gas appeared to evolve. However, this gas evolution was not consistent for all reactions, and ambient-temperature reactions failed to provide significant consumption of substrate over a period of days. To achieve faster reaction times, these mixtures were degassed, heated to 65 °C, and monitored by $^{11}B\{^1H\}$ NMR spectroscopy. Control experiments have demonstrated no appreciable dehydrocoupling occurs under these conditions in the absence of zirconium compounds.[11] Thus, reactions were run for optimal substrate consumption over the shortest period of time at 65 °C; catalysts loadings were initially screened at higher values, typically 5 mol %, then reduced if efficient. Good to excellent percent conversion of amine boranes, generally to corresponding borazines and borazanes, was observed at all loadings, and the best consumptions of substrate for the lowest catalyst loadings are noted here (Table 1). The elevated temperatures and reaction times show that **1** is not as active as several other group 4 metal systems and noble metals, which react in hours at ambient temperature to reach complete conversion. Interestingly, Me_2NHBH_3 and NH_3BH_3 appear to be most rapidly dehydrogenated with **1** despite being sterically hindered and open substrates, respectively.[44] It is important to note that reactions with these substrates were conducted in different solvents due to the poor solubility of NH_3BH_3 in benzene-d_6. Comparing catalytic dehydrogenation of Me_2NHBH_3 between benzene-d_6 and THF-d_8 solutions show the latter to be qualitatively faster, which suggests a polar reaction. Because more detailed product characterization data are available for benzene-d_6, this solvent was chosen for study with alkyl amine boranes. Regardless, the observation of faster reactivity for less sterically encumbered substrates stands in contrast to the general trend reported for group 4 catalysts.[20,21,23,24] Using compound **1**, the dehydrocoupling of $^tBuNH_2BH_3$ is only achieved with modest yields and several days of heating. This relationship is consistent with $(N_3N)Zr$-catalyzed phosphine dehydrocoupling reactions, where reduced catalytic activity for more encumbered substrates was also observed.[45]

Table 1. Amine Borane Dehydrocoupling with 1−4[a]

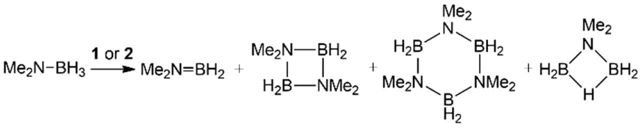
cmpd	substrate	loading (mol %)	% conv[c]	time/d
1	Me_2NHBH_3	0.5	85	4
1	$^tBuNH_2BH_3$	5	79	4
1	NH_3BH_3[b]	1	100	1
2	Me_2NHBH_3	1	100	1
2	$^tBuNH_2BH_3$	1	75	2
2	NH_3BH_3[b]	1	97	2
3	Me_2NHBH_3	1	85	5
3	$^tBuNH_2BH_3$	1	88	5
4	$^tBuNH_2BH_3$[d]	10	100	1

[a] In benzene-d_6, 65 °C. [b] In THF-d_8. [c] Determined by $^{11}B\{^1H\}$ NMR spectroscopy. [d] Reaction not further optimized.

Using the reaction conditions for **1**, other zirconium complexes $(N_3N)ZrR$ (R = NMe_2 (**2**), Cl (**3**), and O^tBu (**4**)) were probed for catalytic activity using 10 equiv of $RR'NHBH_3$. Once similar activity was identified, catalyst loadings were optimized (Table 1). Dehydrocoupled products were readily formed as observed by $^{11}B\{^1H\}$ NMR spectroscopy. Similar yields and catalyst loadings were obtained with these catalyst as with **1**. Because **2** is conveniently prepared,[46] it was used to study the product distribution of amine borane dehydrocoupling reactions by $^{11}B\{^1H\}$ NMR spectroscopy.

Analysis of ^{11}B NMR spectra reveals predominate formation of borazines and borazanes in most reactions, based on comparison to product assignments in the literature (Tables 2−4). In the dehydrocoupling of Me_2NHBH_3, the major product is the diborazane $[NMe_2BH_2]_2$ while trace amounts of amino diborane, $Me_2NHB_2H_5$, and cyclotriborazane, $[NMe_2BH]_3$, are observed (<5%, Table 2).[47] The latter two borazanes are somewhat rarely observed in the literature and are present in only trace amounts in these reactions. The cyclotriborazane is reported to form via metal-catalyzed addition of $Me_2N{=}BH_2$ across $[NMe_2BH_2]_2$, but this addition is reversible under thermodynamic conditions.[21] Further

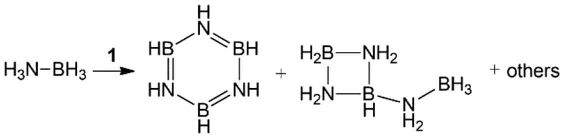
Table 2. Distribution of Products (%) in the Dehydrocoupling of Me_2NHBH_3 by 1 and 2[a]



	$Me_2N{=}BH_2$	$[Me_2NBH_2]_2$	$[Me_2NBH_2]_3$	$Me_2NB_2H_5$
2	2	95	3	0
1	0	94	4	2

[a] In benzene-d_6, at 65 °C, relative product distribution determined by $^{11}B\{^1H\}$ NMR spectroscopy.

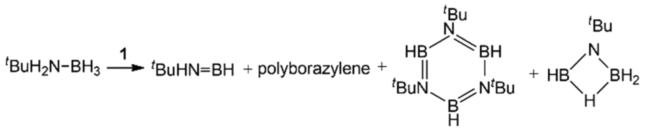
Table 3. Product Distribution (%) in the Dehydrocoupling of NH_3BH_3 by 1[a]



BN	poly-BN	BCDB	δ −3	$[NH_2BH_2]_3$	$[NH_2BH_2]_2$	$NH_2B_2H_5$
40	9	25	7	7	7	5

[a] THF-d_8 solution at 65 °C, relative product distribution determined by $^{11}B\{^1H\}$ NMR spectroscopy; BN = $(NHBH)_3$, poly-BN = polyborazylene, BCDB = B-(cyclodiborazanyl)amine-borane.

Table 4. Distribution of Products (%) in the Dehydrocoupling of $^{t}BuNH_2BH_3$ by 1[a]



$^{t}BuNH{=}BH_2$	poly-^{t}Bu-borazylene	$[^{t}BuNBH]_3$	$\delta - 10$	$^{t}BuNHB_2H_5$
5	21	16	48	10

[a] Benzene-d_6 solution at 65 °C, % determined by $^{11}B\{^{1}H\}$ NMR spectroscopy.

confirmation of the amidoborane intermediate, $Me_2N{=}BH_2$, came from direct observation, albeit in low concentration, in some runs by $^{11}B\{^{1}H\}$ NMR spectroscopy. Therefore, it highly likely that zirconium generates an amido borane intermediate, and then the metal further participates in ring-closure reactions.

In the dehydrocoupling of NH_3BH_3, primarily borazines and borazanes were observed (Table 3). Similar to the dehydrocoupling of Me_2NHBH_3, amino diborane is afforded as well as the borazine and borazane. Significant formation of an insoluble colorless precipitate also formed (~35−50% conversion by mass of solid), suggestive of higher-order oligomers or polybranched polymers, which are known to be insoluble in common organic solvents.[6] Indeed, recently identified intermediate compounds in the polymerization of ammonia borane, including *B*-(cyclotriborazanyl)amine-borane, appear to be present in this reaction.[28] As with Me_2NHBH_3, the products are suggestive of metal-assisted coupling of an amido borane intermediate, but here such an intermediate was not observed.

In contrast, the dehydrocoupling of $^{t}BuNH_2BH_3$ required longer reaction times and afforded lower conversions than those observed for the previous two substrates (Table 4). The major product, which resonates at $\delta = -10$ in the $^{11}B\{^{1}H\}$ NMR spectrum, is unidentified. Other products that are formed include the known triborazine, polyborazylene, and the amino diborane.[48−50] Interestingly, the formation of $^{t}BuNH{=}BH_2$ is also observed in small quantities. It is important to note that there is significant disagreement regarding several assignments of the dehydrcoupling products of $^{t}BuNH_2BH_3$.[51,52] For example, one reviewer noted that the unassigned products around $\delta = -10$ may be isomers of the *tert*-butylaminoborane oligomers.[51] Indeed, it is important to consider these alternative assignments. Most germane to this work, both sets of assignments are consistent with $^{t}BuNH{=}BH_2$ formation and on- and off-metal coupling products.

The identity of the catalytically active species was of interest. In phosphine dehydrocoupling reactions, compound **1** is converted to a phosphido compound via ring-opening of the metallocycle.[45] In the catalytic dehydrocoupling of Me_2NHBH_3 and $^{t}BuNH_2BH_3$, new metal-containing compounds were observed by ^{1}H NMR spectroscopy with resonances similar to those of **2**[46] and $(N_3N)ZrNH^{t}Bu$, respectively.[53] Identifying an analogous compound in the catalytic dehydrocoupling of NH_3BH_3 was more difficult due to overlapping ^{1}H NMR resonances with dehydrocoupling products. Stoichiometric reactions with NH_3BH_3 yielded dehydrocoupling products, and a metal-containing intermediate was not observed.

Because the observed resonances were shifted slightly from the known (N_3N)Zr-amido compounds, it was hypothesized that species of the type $(N_3N)ZrNRR'BH_3$ may be present, and efforts to independently synthesize such derivatives were undertaken. Treatment of **1** with 5 equiv of Me_2NHBH_3 in Et_2O afforded orange crystals of a compound that appear impure by ^{1}H NMR spectroscopy. Extended cooling of reaction mixtures of **1** with Me_2NHBH_3 in Et_2O solution at −35 °C yielded orange block crystals, which were subject to an X-ray diffraction study (Figure 1). The structure, which is indeed that of $(N_3N)ZrNRR'BH_3$ (**5**), confirms that **1** activates amine borane substrates at the N−H bond. Unfortunately, no demonstrative spectroscopic or analytical data to fully support this formulation could be obtained. Compound **5** does represent a relatively rare example of an amidoborane ligand featuring an η^2 sigma borane interaction,[54−59] which may be an important analogue for other group 4 metal catalysts proposed to activate the B−H bonds of amine borane substrates. Zirconium compounds with σ-bond borane ligands, though, are ubiquitous[60−72] and have been structurally characterized for nearly 50 years starting with $Zr(BH_4)_4$.[73,74] The Zr−B distance of η^2 σ-bond compounds is variable, with a good example being the range of distances measured for $Zr\{(\mu\text{-}H)_2BC_8H_{14}\}_4$ of 2.352(2)−2.501(2) Å.[72] The Zr−B distance of **5**, 2.4683(17) Å (Table 5), fits into that range, although it is shorter than many zirconocene compounds with η^2 B−H σ-bond ligands, which are often greater than 2.5 Å.[61−71] That observation is unsurprising given that the dimethylamido fragment has Zr−N = 2.3955(12) Å, which is consistent with an Zr−N σ-bond in these systems[53] and would likely geometrically constrain the borane.

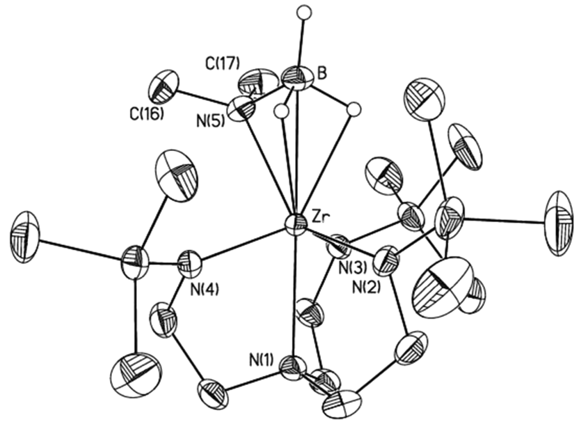


Figure 1. Perspective view of the molecular structure of **5** with thermal ellipsoids shown at the 50% probability level and hydrogen atoms, except those located on B, omitted for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $(N_3N)ZrNMe_2BH_3$ (5)

Zr−B	2.4683(17)	N(5)−B−Zr	69.17(8)
Zr−N(1)	2.4510(12)	C(16)−N(5)−B	110.62(14)
Zr−N(2)	2.1229(13)	C(17)−As(5)−B	115.63(13)
Zr−N(3)	2.1422(12)	N(1)−Zr−B	179.27(5)
Zr−N(4)	2.0438(12)	H(1)−Zr−H(2)	47.8(6)
Zr−N(5)	2.3955(12)	H(1)−B−H(2)	100.7(12)
N(5)−B	1.523(2)	H(1)−B−H(3)	112.9(14)
Zr−H(1)	2.192(18)	H(2)−B−H(3)	115.3(13)
Zr−H(2)	2.219(18)		

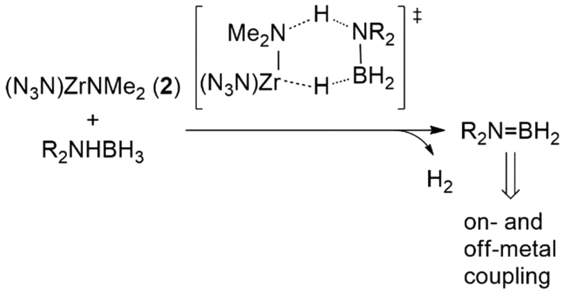
If benzene-d_6 samples of **5** are allowed to stand at ambient temperature, these completely converted to dimethylamido compound **2**, a process accelerated by mild heat (40 °C) or reduced pressure ($\tau \approx 30$ min). It was suspected that the zirconium-containing intermediate formed in the reaction of **1** with Me_2NHBH_3 was $(N_3N)ZrNMe_2BH_3$ (**5**), and catalytic reactions with **1** show spectroscopic data consistent with **2** and not **5** (vide supra). The lability of BH_3 is further supported by the observation that reactions of **2** with THF solutions of BH_3 yielded no evidence of borane association to the amido ligand (i.e., **5**) by ^1H or $^{11}B\{^1H\}$ NMR spectroscopy. This apparent borane lability helps to understand how products with N:B ratios other than 1:1 are obtained (e.g., $Me_2NB_2H_5$). While compound **5** is structurally interesting within the cannon of compounds bearing amido borane ligands, the instability of **5** with respect to loss of borane suggests that this compound is highly unstable under catalytic conditions, where that decomposition process is not productive with respect to the majority of products observed.

Similar procedures did not allow for the isolation of new metal-containing products in stoichiometric reactions of $^tBuNH_2BH_3$ and NH_3BH_3 with **1**. In stoichiometric reactions of **1** with $^tBuNH_2BH_3$, $(N_3N)ZrNH^tBu$ was isolated, which is consistent with the observations for Me_2NHBH_3. The reticence of $(N_3N)Zr$ compounds to undergo β-hydrogen elimination[40] and the apparent instability of any putative amido borane intermediate with respect to borane loss argue against N−H bond activation followed by β-hydrogen elimination. Therefore, the catalysis must proceed by a different pathway.

Compounds **2**−**4** feature pseudoaxial X ligands that form some of the strongest $(N_3N)Zr-X$ bonds described and give no evidence for XH elimination via cyclometalation.[53] Monitoring catalytic reactions of **2**−**4** by ^1H NMR spectroscopy demonstrated that those compounds were preserved throughout the course of these reactions. With increasing product formation, however, some product and catalyst resonances were significantly overlapped. Furthermore, no evidence for protonolysis of the X ligand was observed. For example, in reactions with **4**, ^tBuOH was not detected by ^1H NMR spectroscopy, and reactions with compounds **2** and **3** failed to give evidence of Me_2NH or HCl formation, respectively.

The inability of these $(N_3N)Zr$ compounds to undergo β-hydrogen elimination demands an alternative route to unsaturated intermediates. Therefore, it is proposed that amine borane dehydrocoupling by $(N_3N)Zr$ compounds occurs via an outer-sphere transfer of hydrogen (Scheme 1). Conversion of **1** to amido borane compounds like **2** upon stoichiometric reaction with amine boranes and the preservation of **2**−**4** in catalytic reactions demonstrates that the active catalyst is unlikely to have a vacant coordination site. Additionally, reactivity at the nitrogen lone pair of this family of compounds has been demonstrated.[69] This is a challenging mechanism to establish directly, but the apparent activation of N−H and B−H bonds across Zr−X bonds implied that transfer of H_2 equivalents to unsaturated substrates (i.e., transfer hydrogenation) may also be possible. Indeed, this would be unique reactivity because **1** is not a competent for the hydrogenation of alkenes or alkynes using H_2, although P−P bonds can be catalytically cleaved by **1** with added H_2.[39]

Scheme 1. Proposed Dehydrogenation of Amine Boranes by 2[a]



[a]Transfer facilitated by the dimethylamido ligand is depicted, but any of the three pseudoequatorial amide arms of the triamidoamine ligand may be competent for this reactivity.

The inability of these compounds to undergo or even form compounds susceptible to β-hydrogen elimination demands an alternative route to unsaturated intermediates. Therefore, it is proposed that amine borane dehydrocoupling by $(N_3N)Zr$ compounds occurs via an outer-sphere transfer of hydrogen (Scheme 1). Conversion of **1** to amido borane compounds like **2** upon stoichiometric reaction with amine boranes and the preservation of **2**−**4** in catalytic reactions demonstrates that the active catalyst is unlikely to have a vacant coordination site. Additionally, reactivity at the nitrogen lone pair of this family of compounds has been demonstrated.[75] This is a challenging mechanism to establish directly, but the apparent activation of N−H and B−H bonds across Zr−X bonds implied that transfer of H_2 equivalents to unsaturated substrates (i.e., transfer hydrogenation) may also be possible. Indeed, this would be unique reactivity because **1** is not a competent for the hydrogenation of alkenes or alkynes using H_2, though P−P bonds can be catalytically cleaved by **1** with added H_2.[40]

Transfer Hydrogenation Reactions. Because Me_2NHBH_3 is commonly used as a hydrogen donor in transfer hydrogenation reactions and **2** is a simple compound to prepare, these reagents were used in initial assays for the hydrogenation of styrene. Reactions at 10 mol % loading of **1** with equimolar styrene and Me_2NHBH_3 give limited conversions to ethylbenzene, despite significant efforts at optimization. These reactions were plagued by rapid dehydrogenation of the amine borane without transfer of hydrogen.

Because dehydrogenation of $^tBuNH_2BH_3$ is relatively slow, this sacrificial donor was next screened. Here, some formation of ethylbenzene was observed in reactions with styrene, but apparent hydroboration products were also observed. Indeed, competitive hydroboration of amines is a known reaction for these kinds of catalysis.[3,76] Because the potential hydroboration byproducts were minor and difficult to fully characterize, the competence of **2** for hydroboration was tested to assess if this is a potential competing reaction in this system. Styrene was treated with catecholborane in the presence of 5 mol % of **2** in benezene-d_6. While hydroborylation was not efficient, it was clear that the hydroborylated product[77] was formed and that **2** is at least competent for this kind of catalysis.

Due to the difficulties faced with alkyl amine boranes, NH_3BH_3 was probed as a hydrogen donor. Using this substrate, product identification was readily accomplished with $^{13}C\{^1H\}$ NMR spectroscopy. Because ammonia borane is dehydrocoupled relatively rapidly, the catalyst loadings for the transfer hydrogenation reactions were decreased to 2 mol %. The reactions proceeded quickly, typically reaching completion after 6 h at 65 °C, as indicated by consumption of the alkene substrate. Initial substrates included styrene and substituted styrene derivatives, alpha olefins, 2,3-dimethylbutadiene, and 2-

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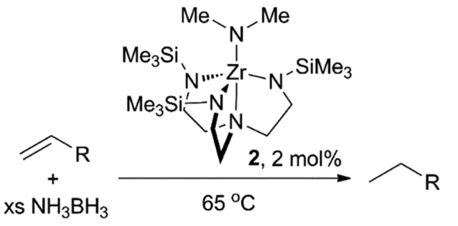
vinylpyridine. All alkene substrates were completely consumed, and the alkane was the major product in all cases. In some instances byproducts consistent with hydroboration were also noted.



(1)

The success of these proof-of-concept hydrogenation reactions demanded that further control reactions be performed. Reactions in which a mixture of **2** and styrene was treated with 1 atm of hydrogen gas at 65 °C for extended periods resulted in no detectable ethylbenzene. This observation demonstrates that amine boranes are required for catalysis as the sacrificial hydrogen source. Another alternative is that **2** acts only as a precatalyst, yielding catalytically active **1** after elimination of Me_2NH. This amine was not observed by ^1H NMR spectroscopy during catalytic reactions, and **2** is persistent at the end of catalysis. Reaction of styrene, as well as the other substrates in this study, with 5 mol % of **1** under 1 atm of hydrogen gas did not yield detectable quantities of hydrogenation products. Indeed, **1** was consumed in these reactions; it is already known that **1** reacts with unsaturated molecules via insertion into the Zr−C bond.[78] From these experiments, it is clear that the amine borane is necessary for hydrogenation and that **1** is not the active catalyst. Thus, these reactions appear to represent the first examples of homogeneous group 4 metal compounds engaging in transfer hydrogenation.

■ CONCLUDING REMARKS

Amine boranes have been dehydrocoupled using triamidoamine-supported zirconium complexes **1**−**4**. The compounds studied in this report were particularly active toward the secondary amine borane, Me_2NHBH_3, and ammonia borane, proceeding at moderate temperatures and reaction times. Indirect evidence provides indications of an outer-sphere-type mechanism. Further support for this hypothesis comes from a preliminary study of compound **2** as transfer hydrogenation catalyst for alkenes using amine boranes as the sacrificial hydrogen source.

Although these are preliminary studies, these compounds demonstrate reasonable activity, and lower catalyst loadings appear to suppress competitive hydroboration reactions. Interestingly, this work is a rare example of group 4 metal catalyzed hydrogenation[21,38] and, in particular, transfer hydrogenation.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under a nitrogen atmosphere with dry, oxygen-free solvents using an M. Braun glovebox or standard Schlenk techniques. Benzene-d_6 was degassed and dried over NaK alloy. Anhydrous THF-d_8 was used as received. ^1H, $^{11}B\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Ascend 500 MHz NMR spectrometer. Reported ^1H NMR resonances are referenced to residual solvents (benzene-d_6 = δ 7.16, THF-d_8 = δ 1.72 or 3.58). Reported $^{13}C\{^1H\}$ NMR resonances are referenced to solvents (benzene-d_6 = δ 128.06, THF-d_8 = δ 67.21 or 25.31). All chemicals were either synthesized from literature methods or purchased from commercial suppliers and dried by conventional means. The syntheses of **1**,[53] **2**,[45] and **3**[46] have been reported. For pertinent NMR spectra, see the Supporting Information.

Amine Borane Dehydrocoupling. All reactions were conducted using a J-Young-type polytetrafluoroethylene (PTFE)-valved NMR tube in benzene-d_6 or THF-d_8. The solution was frozen and the headspace evacuated. This was repeated at regular intervals during the course of the reaction to remove H_2. After thawing, the NMR tube was heated at 65 °C. All NMR spectra were collected at 25 °C. The reactions were monitored using ^1H and $^{11}B\{^1H\}$ NMR spectroscopy. Dehydrocoupling products of NH_3BH_3, Me_2NHBH_3, and $^tBuNH_2BH_3$ were identified by their reported ^{11}B NMR chemical shifts as compared to the unreacted ammonia borane as an internal reference.[1,2]

Catalyst was dissolved in deuterated solvent, and the amine borane was added to the colorless solution (Table 6). Almost immediate formation of H_2 gas was observed, although the solution remained colorless. With increased time, a fine precipitate was observed in the dehydrocoupling of the ammonia borane.

Table 6. Optimized Reaction Conditions of Amine Boranes with Compounds 1−4

cmpd	amine borane
1, 2.3 mg, 0.0050 mmol	Me_2NHBH_3, 63 mg, 1.1 mmol
1, 6.7 mg, 0.015 mmol	$^tBuNH_2BH_3$, 27 mg, 0.31 mmol
1, 9.3 mg, 0.021 mmol	NH_3BH_3, 69 mg, 2.2 mmol
3, 4.8 mg, 0.010 mmol	Me_2NHBH_3, 66 mg, 1.1 mmol
3, 8.1 mg, 0.017 mmol	$^tBuNH_2BH_3$, 148 mg, 1.7 mmol
4, 4.8 mg, 0.0092 mmol	$^tBuNH_2BH_3$, 8.9 mg, 0.10 mmol
2, 4.1 mg, 0.0085 mmol	Me_2NHBH_3, 49 mg, 0.85 mmol
2, 4.4 mg, 0.0089 mmol	$^tBuNH_2BH_3$, 78 mg, 0.90 mmol
2, 6.5 mg, 0.013 mmol	NH_3BH_3, 38 mg, 1.2 mmol

Transfer Hydrogenation Reactions. All reactions were conducted using a J-Young-type PTFE-valved NMR tube in benzene-d_6 or THF-d_8. Reagents were combined with solvent in the NMR tube (Table 7), the solution was frozen, and the headspace was evacuated. Unless otherwise noted, all reactions were heated at 65 °C and were monitored using ^1H, $^{11}B\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy. Hydrogenation products were identified by ^{13}C NMR chemical shifts in comparison to literature values.

Table 7. Procedures for Hydrogenation of Unsaturated Substrates with 2

cmpd **2**	substrate	NH_3BH_3
15 mg, 0.030 mmol	styrene 250 mg, 2.40 mmol	73 mg, 2.35 mmol
16 mg, 0.032 mmol	4-methoxystyrene 370 mg, 2.76 mmol	81 mg, 2.61 mmol
10 mg, 0.020 mmol	2-vinylpyridine 116 mg, 1.10 mmol	31 mg, 1.0 mmol
8.9 mg, 0.018 mmol	ethyl vinyl ether 60 mg, 0.83 mmol	24 mg, 0.77 mmol
6.7 mg, 0.014 mmol	2,3-dimethyl butadiene 18 mg, 0.22 mmol	14 mg, 0.45 mmol
15 mg, 0.030 mmol	*tert*-butylethene 54 mg, 0.64 mmol	19 mg, 0.62 mmol
8.1 mg, 0.016 mmol	1-hexene 69 mg, 0.82 mmol	28 mg, 0.9 mmol

X-ray Structure Determinations. X-ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometer (Mo Kα, λ = 0.710 73 Å) at 125 K. Suitable crystals of **5** were mounted in a nylon loop with Paratone-N cryoprotectant oil. The structure was solved via direct methods with standard difference map techniques and refined by full-matrix least-squares procedures on F^2 with SHELXTL (version 6.14).[79] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and were refined using a riding model. The hydrogen atoms on boron, H(1), H(2), and H(3), were located in the Fourier difference map and refined freely. Crystal data and refinement details are presented in Table S9.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00415.

Representative NMR spectra of catalytic reactions (PDF)
A CIF file with X-ray crystal structure data for compound **5** (CIF)

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Gregory L. Hillhouse (1955–2014) was many things to many people. We dedicate this paper to his caring mentorship and his love of "hot, new results".

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