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Homogeneous Catalytic Dehydrocoupling/Dehydrogenation of Amine−Borane Adducts by Early Transition Metal, Group 4 Metallocene Complexes

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Abstract: The efficient catalytic dehydrocoupling of a range of amine−borane adducts, $R'RNH\cdot BH_3$ ($R' = R = Me$ **1a**; $R' = R = {}^iPr$ **1b**; $R' = Me$, $R = CH_2Ph$ **1c**) by a series of group 4 metallocene type precatalysts has been demonstrated. A reduction in catalytic activity was detected upon descending the group and also on substitution of the cyclopentadienyl (Cp) ligands with sterically bulky or electron-donating substituents. Precatalysts $Cp_2TiCl_2/2{}^nBuLi$ and $Cp_2Ti(PMe_3)_2$, which are believed to act as precursors to $[Cp_2Ti]$, were found to promote the transformation of **1a** to $[Me_2N\text{-}BH_2]_2$ (**3a**) in a homogeneous catalytic process. Mechanistic studies identified the linear dimer $Me_2NH\text{-}BH_2{-}NMe_2\text{-}BH_3$ (**2a**) as a reaction intermediate, which subsequently undergoes further catalytic dehydrogenation to form cyclic dimer **3a**. Synthesis of the ^2H-isotopologues of **1a** allowed the extraction of phenomenological kinetic isotope effects for **1a** → **2a** and **2a** → **3a** from initial rate data, which permitted the proposal of a catalytic cycle with plausible intermediates. Support for the presence of an active Ti(II) catalyst was provided by the lack of reactivity of Ti(III) complexes $TiCl_3$ and Cp_2TiCl or Ti(0) in the form of THF soluble colloids or bulk Ti powder toward **1a** or **1b**. Modeling of the rates of consumption of **1a** and formation of **3a** during catalysis by $Cp_2Ti(PMe_3)_2$ supported this conclusion and allowed the proposal of a two cycle, four step reaction mechanism. The proposed first cycle generates **2a** in a two step process. In the second cycle, interaction of **2a** with the same catalyst then results in a catalytic dehydrogenative ring closing reaction to form **3a**, also in a two step process.

Introduction

The use of transition metal complexes as catalysts to effect the synthesis and transformations of organic molecules through C−X (X = C, N, or O) bond formation and polymerization processes is a thoroughly developed area of profound current importance. By comparison, the use of catalytic reactions to prepare catenated inorganic species is still in its relative infancy, with the formation of main group element−element bonds relying almost entirely on salt elimination reactions. Since the initial reports of transition metal catalyzed formation of B−B and Si−Si bonds via dehydrogenative coupling by Sneddon[1] and Harrod[2] in the 1980s, the area has expanded to include a range of homonuclear and heteronuclear bond forming reactions, allowing convenient access to main group based rings, chains and high molecular weight polymers.[3] Moreover, with current intense interest in the potential of a hydrogen economy to provide a clean source of energy, amine−borane adducts such as $NH_3\cdot BH_3$ (**1e**) are under detailed scrutiny as potential safe and stable hydrogen storage materials.[4−9,16c]

We have previously reported the Rh-catalyzed dehydrocoupling of phosphine−borane adducts by late transition metal precatalysts such as $[Rh(\mu\text{-}Cl)(1,5\text{-}cod)]_2$ to yield a range of

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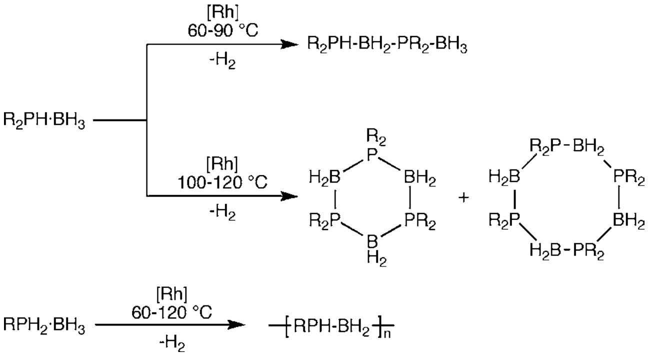
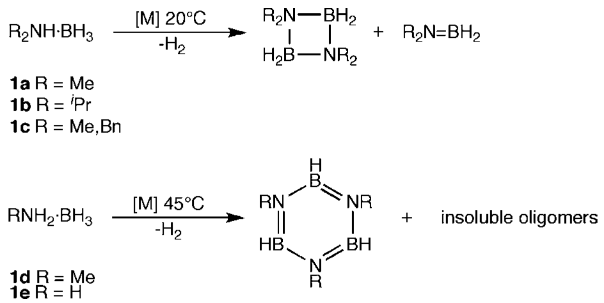
Scheme 1. Catalytic Dehydrocoupling of Primary and Secondary Phosphine−Borane Adducts by Rh Precatalysts (e.g., $[Rh(\mu\text{-}Cl)(1,5\text{-}cod)]_2$)



Scheme 2. Catalytic Dehydrocoupling of Primary and Secondary Amine−Borane Adducts by Transition Metal Precatalysts (Bn = CH_2Ph)



linear (at 60−90 °C) and cyclic products (at 100−120 °C), in the case of secondary phosphine−borane adducts, and high molecular weight polymers in the case of primary phosphine−borane adducts (Scheme 1). Detailed studies of these reactions suggested that the active catalyst is homogeneous, an assertion consistent with nanofiltration, colloidal catalyst poisoning, and other studies.[10−13]

We subsequently reported the extension of this catalytic dehydrocoupling/dehydrogenation chemistry to primary and secondary amine−borane adducts, and to **1e** (Scheme 2). Thus, in the presence of a variety of late transition metal precatalysts such as $[Rh(\mu\text{-}Cl)(1,5\text{-}cod)]_2$, a range of cyclic oligomeric or insoluble polymeric species were formed either at or slightly above ambient temperature.[14,15] Mechanistic studies indicated that, in the case of $[Rh(\mu\text{-}Cl)(1,5\text{-}cod)]_2$ as a precatalyst, the dehydrogenation of $Me_2NH\cdot BH_3$ (**1a**) to form the cyclic dimer $[Me_2N\text{-}BH_2]_2$ (**3a**) proceeds via reduction to Rh(0) species and the true catalyst appears to be heterogeneous in nature.[11,16] Recent advances reported by a range of research groups have led to the discovery of new and improved late (Fe, Ni,[6] Rh,[9,17,18] Ir[5,19]), mid (Re,[20] Ru[7,8]) and early (Cr, Mo, W[21]) transition metal catalysts for the dehydrogenation of amine−borane adducts such as **1a** or **1e**. Many of these catalytic reactions are substrate specific and the mechanisms of the dehydrocoupling/dehydrogenation processes are of key importance. In some cases mechanistic insight has recently been provided by computational studies and the isolation of potential intermediates.[4a,8,9,22]

As part of our efforts to expand the range of transition metal catalysts for amine−borane dehydrogenation we have explored the use of group 4 metallocene complexes. Such systems have previously been shown to be active for the dehydrocoupling/dehydrogenation of silanes such as $PhSiH_3$.[2,23] In 2006, we briefly reported that $[Cp_2Ti]$, generated *in situ* from $Cp_2TiCl_2/2^nBuLi$ at −15 °C with subsequent warming to 20 °C, functions as an efficient *homogeneous* catalyst for the dehydrocoupling of secondary amine−borane adducts such as **1a**.[24] A subsequent computational investigation of this system by Ohno and Luo suggested that the mechanism involved an intramolecular, stepwise process.[25] These workers suggested that **1a** initially interacts with the catalytic metal center via a B−H bond, followed by proton transfer from nitrogen and subsequent hydride transfer from boron to give the dehydrogenated aminoborane $Me_2N{=}BH_2$ (**5a**) and Cp_2TiH_2. They proposed that the former then dimerizes in an *uncatalyzed* manner while the resulting titanocene dihydride releases hydrogen to reform $[Cp_2Ti]$ (Scheme 3). In a further development, Chirik and coworkers reported the dehydrocoupling of **1a** and **1e** by a series of other group 4 complexes and observed that increased substitution of the Cp ligands resulted in reduced catalytic activity.[26] Signficantly, a N_2 complex $[\{(1,3\text{-}(SiMe_3)_2C_5H_3)_2Ti\}_2(\eta^1\text{-}N_2)]$ was found to be a highly efficient catalyst for **1a** and a mechanism involving initial B−H oxidative addition was proposed.

In this paper, as a follow up to our preliminary communication,[24] we report a detailed study of the catalytic dehydrocoupling of amine−borane adducts by group 4 transition metal

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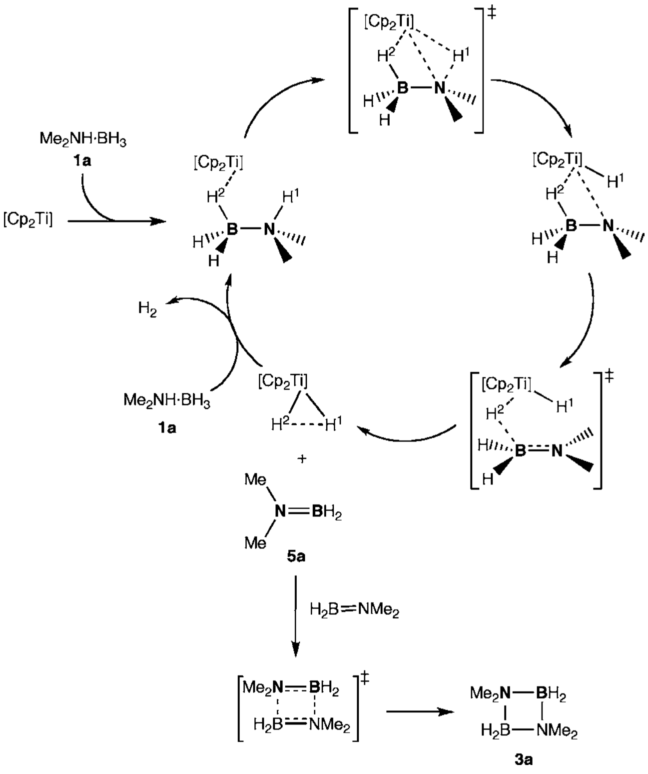
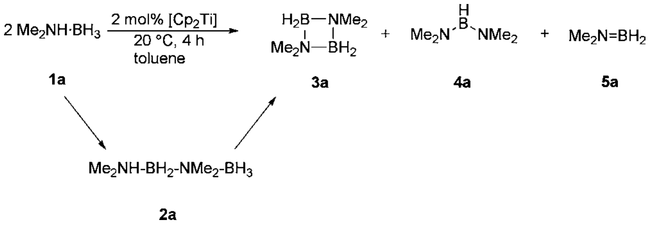
Scheme 3. Intramolecular Stepwise Catalytic Dehydrocoupling of **1a** by [Cp_2Ti] Proposed by Ohno and Luo[25]



Scheme 4. Catalytic Dehydrocoupling of **1a** by [Cp_2Ti] to Afford **2a** and **3a**



metallocene complexes. Our work includes in-depth kinetic and mechanistic studies that provide new insight into the pathways involved for this interesting early transition metal-catalyzed process.

Results

1. Catalytic Dehydrocoupling of $Me_2NH \cdot BH_3$ (1a) with $Cp_2TiCl_2/2^nBuLi$. To investigate if catalysts of the type [Cp_2Ti] would be active for the dehydrocoupling of amine−borane adducts, a toluene solution of $Me_2NH \cdot BH_3$ (**1a**) was treated with a catalytic amount (2 mol %) of [Cp_2Ti] generated *in situ*. Extensive H_2 release was observed, which was confirmed by ^1H NMR spectroscopy ($\delta(^1H) = 4.46$ in C_6D_6 lit. 4.46)[27] along with full conversion of **1a** to yield **3a** as the dominant product after 4 h, as determined by ^{11}B NMR spectroscopy (Scheme 4).[28]

The exact details of the reaction between Cp_2TiCl_2 and ^nBuLi are not known with certainty but it has been proposed that

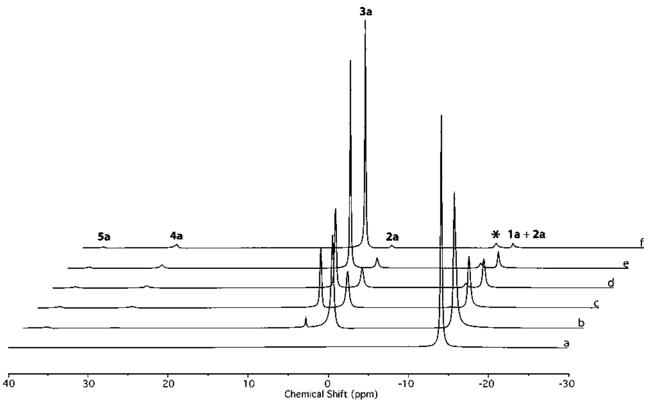


Figure 1. $^{11}B\{^1H\}$ NMR (96 MHz, unlocked, toluene) spectrum showing conversion of **1a** (1.3 M in toluene) to **2a** and **3a** by [Cp_2Ti] generated *in situ* (2 mol % in toluene), * = unidentified species. (a) $t = 0$ min, (b) $t = 15$ min, (c) $t = 75$ min, (d) $t = 95$ min, (e) $t = 135$ min, (f) $t = 240$ min.

$Cp_2Ti^nBu_2$ is generated first, followed by the formation of the putative Ti(II) product "Cp_2Ti" via a β-hydrogen elimination/reductive elimination and olefin dissociation pathway.[29,30] Presumably the electron-deficient, coordinatively unsaturated Ti center in the latter facilitates an initial reaction with **1a** and entry into the catalytic cycle. The proposed involvement of Ti(II) is reinforced by the report of Sneddon and co-workers describing that hydroboration reactions of decaborane, $B_{10}H_{14}$, with terminal olefins can be promoted by the Ti(II) precatalyst $Cp_2Ti(CO)_2$.[31]

During the course of the catalytic dehydrocoupling of **1a**, to generate **3a**, the formation of several other boron-containing species was noted in the $^{11}B\{^1H\}$ NMR spectrum. In the early stages, a signal at δ 2 ppm was observed. This signal corresponds to the internal BH_2 moiety in the linear dimer Me_2NH-BH_2−NMe_2-BH_3 (**2a**), as confirmed by comparison with an authentic sample of this species. Linear dimer **2a** appears to be an intermediate in the dehydrocoupling of **1a** (Figure 1).[7b,32−34] This signal split into a triplet when the ^1H coupled ^{11}B NMR spectrum was recorded ($^1J_{B-H} = 108$ Hz), while the signal for the terminal BH_3 unit was obscured by the signal for starting material **1a** (see Figure S1 and S2, Supporting Information). The intensity of this signal (δ 2 ppm) increased rapidly for the first 15 min of the reaction, but subsequently decreased as **3a** is formed. Small signals were also noted in the spectrum at δ 28 ppm (d, $^1J_{B-H} = 130$ Hz), which was assigned to the

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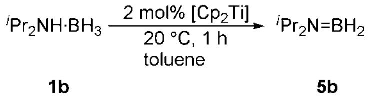
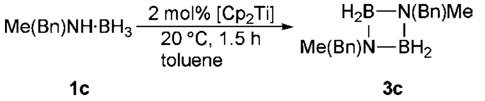
(33) In our preliminary communication (ref 24) we tentatively postulated a cyclic trimer structure, $[Me_2N\text{-}BH_2]_3$, for the intermediate based on our observation of unresolved ^1H coupled and decoupled ^{11}B NMR spectra in toluene (see Figure S1, Supporting Information). Our further studies and private communication with S. Schneider (T. U. Munich) revealed this assignment to be incorrect. The ^{11}B NMR signals can be resolved in C_6D_6 (see Figure S2, Supporting Information). For further relevant discussions of the same issues see refs 7b and 18. It should also be noted that the coupling constants reported for linear dimer Me_2NH-BH_2−NMe_2-BH_3 in ref 32 are incorrect. The correct values are ^{11}B NMR (96 MHz, C_6D_6, 20 °C) $\delta -13.2$ (q, $^1J_{BH} = 96$ Hz), 2 (t, $^1J_{BH} = 108$ Hz) (see Supporting Information S1 and S2).

(34) The catalytic conversion of **2a** to **3a** has previously been reported using Rh(0) catalysts (see ref 15).

Scheme 5. Dehydrocoupling of **1b** by $Cp_2TiCl_2/2^nBuLi$ to Give **5b**



Scheme 6. Dehydrocoupling of **1c** by $Cp_2TiCl_2/2^nBuLi$ to Give **3c**

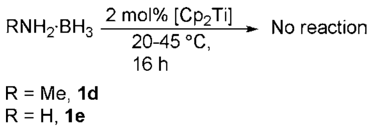


diaminoborane $(Me_2N)_2BH$ (**4a**),[35] and at δ 37 ppm, which was tentatively assigned to monomeric **5a**, a possible precursor to both **3a** and **2a**.[36] The generation of a very small amount of an unidentified species was also noted at $\delta(^{11}B)$ −11.6 ppm. Interestingly, addition of an independently synthesized sample of **2a**[15] to a catalytic amount of [Cp_2Ti], generated from $Cp_2TiCl_2/2^nBuLi$, resulted in complete consumption of **2a** and conversion to **3a** (98%), **4a** (~1%) and **5a** (~1%) after 4 h. A detailed discussion of the kinetics of the dehydrocoupling of **1a** by [Cp_2Ti] generated from an alternative precatalyst $Cp_2Ti(PMe_3)_2$, is presented later (Section 5).

2. Catalytic Dehydrocoupling of Other Amine−Borane and Phosphine−Borane Adducts with $Cp_2TiCl_2/2^nBuLi$. We also investigated the catalytic activity of [Cp_2Ti] toward more sterically encumbered amine−borane adducts. Treatment of $^iPr_2NH{\cdot}BH_3$ (**1b**) and MeBnNH·BH_3 (Bn = CH_2Ph) (**1c**), with a catalytic amount of [Cp_2Ti] resulted in full conversion to $^iPr_2N{=}BH_2$ (**5b**) and $[MeBnN\text{-}BH_2]_2$ (**3c**) in 1 and 1.5 h respectively (Schemes 5 and 6). By comparison, we have previously shown that **1b** dehydrogenates much more slowly in the presence of a Rh(I) precatalyst such as [Rh(μ-Cl)(1,5-cod)]$_2$ (1 mol %, 25 °C, neat, 92% conversion to **5b** after 96 h).[15]

In a further effort to examine the scope of the Ti-catalyzed dehydrocoupling reaction toward other related species, the reactivity of the primary amine−borane adducts $MeNH_2{\cdot}BH_3$ (**1d**) and $NH_3{\cdot}BH_3$ (**1e**) was explored. Previous work has shown that upon treatment with Rh precatalysts at 45 °C these amine−borane adducts yield borazines $[RN\text{-}BH]_3$ (R = Me, H), presumably via the borazanes $[RNH\text{-}BH_2]_3$, together with insoluble, presumably cross-linked oligomeric material.[15] In contrast to **1a**, species **1d** showed negligible reaction by ^{11}B NMR spectroscopy upon treatment with 2 mol % [Cp_2Ti], yielding less than 1% $[MeNH\text{-}BH_2]_3$ after 16 h at 20 °C. Furthermore, **1e** showed no conversion at all under the same conditions in diglyme and also at elevated temperatures (45 °C, 16 h) (Scheme 7).[37,38]

Scheme 7. Attempted Dehydrocoupling of Primary Amine−Borane Adducts by [Cp_2Ti]



In an attempt to further expand the scope of the Ti-catalyzed reaction, the catalytic dehydrocoupling of the secondary phosphine−borane adduct $Ph_2PH{\cdot}BH_3$ was also investigated. Phosphine−borane adducts generally undergo catalytic dehydrocoupling with Rh catalysts at more elevated temperatures (60−120 °C). It therefore appeared likely that the thermal instability[38] of the [Cp_2Ti] catalyst might provide a fundamental limitation in this area. Indeed, treatment of $Ph_2PH{\cdot}BH_3$ with 2 mol % [Cp_2Ti] at 20 or 40 °C resulted in no detectable reaction in either case, according to ^{31}P and ^{11}B NMR spectroscopy. We have previously described the use of electron-withdrawing fluorinated aryl substituents at the phosphorus center of phosphine−borane adducts as a means of lowering catalytic dehydrocoupling reaction temperatures through activation of the P−H bond through an inductive effect.[13] With this in mind, the Ti-catalyzed dehydrocoupling of the primary phosphine−borane adduct (p-$CF_3C_6H_4$)$PH_2{\cdot}BH_3$ was also attempted at 20 and 40 °C; however, again no reaction was detected in either case.

To further investigate the scope of group 4 catalysts we moved on to explore related species in an attempt to find systems with comparative or superior catalytic activity.

3. Attempted Dehydrocoupling of 1a and 1b with Other Group 4 Precatalysts. (a) Attempted Catalytic Dehydrocoupling with [Cp_2Zr] and [Cp_2Hf]. Due to the high catalytic activity exhibited by [Cp_2Ti], we also investigated the activity of analogous group 4 metal complexes. Treatment of a toluene solution of Cp_2ZrCl_2 with 2 equivalents of ^nBuLi at −15 °C, and subsequent addition of **1a** or **1b** resulted in no reaction, as observed by $^{11}B\{^1H\}$ NMR spectroscopy. On changing the reaction solvent to THF, again no reaction was observed for **1a** after 20 h; however, 65% conversion of **1b** to **5b** was detected after 20 h by ^{11}B NMR spectroscopy.[39,40] By comparison, treatment of **1a** or **1b** with [Cp_2Hf], generated in a manner analogous to [Cp_2Zr], resulted in no reaction in both cases (Table 1).[41] This highlights the decrease in catalytic activity associated with descending the group, a result also noted by Chirik and co-workers.[26]

(b) Attempted Dehydrocoupling with [$Me_2Si(\eta^5\text{-}C_5H_4)_2M$] (M = Ti or Zr). The dimethylsilyl-*ansa*-dichloro-metallocene $Me_2Si(\eta^5\text{-}C_5H_4)_2MCl_2$ can be isolated as dark red-brown and pale yellow-green crystals for M = Ti or Zr, respectively.[42] Treatment of a toluene solution of $Me_2Si(\eta^5\text{-}C_5H_4)_2TiCl_2$ with two equivalents of ^nBuLi at −15 °C, and subsequent warming to 20 °C resulted in the formation of a pale-yellow solution. Addition of **1a** resulted in a color change to brown, with a small amount of gas evolution. $^{11}B\{^1H\}$ NMR analysis of an aliquot

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(35) (a) Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance of Boron Compounds*; Springer-Verlag: Berlin, 1978. (b) Srivastava, D. K.; Krannich, L. K.; Watkins, C. L. *Inorg. Chem.* **1991**, *30*, 2441–2444.

(36) Nöth, H.; Vahrenkamp, H. *Chem. Ber.* **1967**, *100*, 3353–3362.

(37) No stoichiometric reaction was observed for **1d** or **1e**.

(38) This apparent lack of catalytic activity over time and at temperatures greater than 20 °C may be attributed to the instability of [Cp_2M] (M = group 4 metal) in solution, which has been well-documented, see: Negishi, E. I. *Dalton Trans.* **2005**, 827–848.

(39) By comparison to the stoichiometric addition of **1a** or **1b** to [Cp_2Ti], which results in fast conversion to **3a** and **5b,** addition of a stoichiometric amount of **1a** or **1b** to [Cp_2Zr] resulted in the formation of several new products in each case. The characterization of these products is ongoing and will be the subject of a future publication. No reaction was observed upon addition of $Me_3N{\cdot}BH_3$ to either [Cp_2Ti] or [Cp_2Zr].

(40) In contrast to the solvent dependence observed for [Cp_2Zr], full conversion of **1a** to **5a** by [Cp_2Ti] required the same time, independent of the solvent choice (toluene or THF).

(41) The lack of reactivity of [Cp_2Hf] is perhaps unsurprising, as $Cp_2Hf(nBu)_2$ has been shown to be an isolable complex at room temperature, which is only reactive at high temperatures (100 °C), see: Burlakov, V. V.; Beweries, T.; Bogdanov, V. S.; Arndt, P.; Baumann, W.; Petrovskii, P. V.; Spannenberg, A.; Lyssenko, K. A.; Shur, V. B.; Rosenthal, U. *Organometallics* **2009**, *28*, 2864–2870.

(42) Bajgur, C. S.; Tikkanen, W.; Petersen, J. L. *Inorg. Chem.* **1985**, *24*, 2539–2546.

Table 1. Summary of Catalyst Screening for the Dehydrocoupling of **1a** (to **3a**) and **1b** (to **5b**) (see Schemes 4 and 5)

	conversion of **1a**		conversion of **1b**	
precatalyst	time (h)	yield (%)[f]	time (h)	yield (%)[f]
Cp_2TiCl_2[a,b]	4	100	1	100
Cp_2ZrCl_2[c,d]	20	0	20	65
Cp_2HfCl_2[c,d]	20	0	20	0
$Cp_2Ti(PMe_3)_2$[a]	7	100	2	100
$Me_2Si(C_5H_4)_2TiCl_2$[a]	20	50	20	100
$Me_2Si(C_5H_4)_2ZrCl_2$[a]	20	0	20	0
$Cp^s{}_2Ti$[a,i]	20	0	20	0
Cp_2TiCl[a] or $TiCl_3$[a]	48	0	48	0
Ti (100 mesh)[e] or Ti colloid	48	0	48	0
$[Rh(\mu\text{-}Cl)(1,5\text{-}cod)]_2$[15]	8	100[g]	96	92[h]

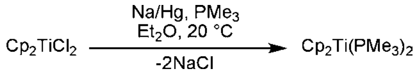
[a] Reaction carried out with 4 mmol of adduct and 2 mol % precatalyst in 3 mL toluene at 20 °C. [b] Full consumption of **1a** and **2a** was observed in the same time period when the reaction was carried out in THF. [c] Reaction carried out with 4 mmol of adduct and 5 mol % precatalyst in 3 mL THF at 20 °C. [d] No reaction of **1a** or **2a** was observed with toluene as the reaction solvent. [e] Reaction carried out with 4 mmol of adduct and 10 mol % precatalyst in 3 mL toluene at 20 °C. [f] Conversion to **3a** or **5b** by integration of $^{11}B\{^1H\}$ NMR spectrum, all reactions were carried out three times with reproducible yields. [g] Reaction carried out with 3.3 mmol of adduct and 0.5 mol % precatalyst in 2 mL toluene at 25 °C (see ref 14). [h] Reaction carried out with 19 mmol of adduct and 1 mol % precatalyst, neat at 25 °C (see ref 14). [i] $Cp^s = (\eta^5\text{-}(C_5Me_4(SiMe_2{}^tBu)))$.

after 20 h indicated 50% conversion to **3a**. By comparison treatment of **1b** with a catalytic amount of $[Me_2Si(\eta^5\text{-}C_5H_4)_2Ti]$ (2 mol %) resulted in 100% conversion to **5b** after 20 h. In accordance with the decrease in reactivity of Zr catalysts compared to those of Ti noted earlier,[26] no reaction was observed on addition of **1a** or **1b** to $[Me_2Si(\eta^5\text{-}C_5H_4)_2Zr]$, generated in either toluene or THF.

(c) Attempted Dehydrocoupling of 1a and 1b with $Cp^s{}_2Ti$ ($Cp^s = \eta^5\text{-}(C_5Me_4(SiMe_2{}^tBu))$). The assembly of a catalyst *in situ* can lead to problems with reproducibility and handling. It is therefore prudent to identify a single component catalyst or precatalyst, which can be added directly to the substrate. One of the few stable Ti(II) complexes, $Cp^s{}_2Ti$ ($Cp^s = (\eta^5\text{-}C_5Me_4(SiMe_2{}^tBu))$), was reported by Lawless and co-workers, and can be isolated as red crystals.[30] A report by Chirik and co-workers highlighted the decrease in catalytic activity of group 4 complexes with highly substituted cyclopentadienyl ligands toward amine−borane adducts.[26] We also observed that an extremely crowded Ti(II) center resulted in very inefficient dehydrocoupling. Thus, treatment of **1a** with 2 mol % of $Cp^s{}_2Ti$ led to no conversion to **3a** after 92 h as observed by $^{11}B\{^1H\}$ NMR spectroscopy. Analogous treatment of **1b** with a catalytic amount (2 mol %) of $Cp^s{}_2Ti$ resulted in only 5% conversion to **5b** after 92 h.

(d) Catalytic Dehydrocoupling of 1a and 1b with $Cp_2Ti(PMe_3)_2$. To access an active and isolable precatalyst, the known Ti(II) complex $Cp_2Ti(PMe_3)_2$[43] was explored. A slightly modified literature procedure was used to prepare this species, with replacement of the reaction solvent (THF) by diethyl ether preventing decomposition upon workup, allowing pure (by ^1H, ^{13}C and ^{31}P NMR spectroscopy) $Cp_2Ti(PMe_3)_2$ to be isolated as a dark red/brown microcrystalline solid without the need for further purification[44] (Scheme 8).

Scheme 8. Synthesis of $Cp_2Ti(PMe_3)_2$



Addition of a catalytic amount (2 mol %) of $Cp_2Ti(PMe_3)_2$ to a solution of **1a** or **1b** in toluene resulted in full conversion to **3a** and **5b** in 7 and 2 h, respectively (Table 1). As in the case of the $Cp_2TiCl_2/2{}^nBuLi$ system, the appearance of a signal corresponding to **2a** early in the reaction, and subsequent conversion to **3a** was observed by $^{11}B\{^1H\}$ NMR spectroscopy, as well as the formation of small amounts of **4a** and **5a** (Figure 2).

(e) Attempted Dehydrocoupling of 1a and 1b with Potential Ti(III) Precatalysts. While it seems likely that catalytic systems $Cp_2TiCl_2/2{}^nBuLi$ and $Cp_2Ti(PMe_3)_2$ both form an active Ti(II) species, it was also important to consider the potential role of Ti(III) complexes. To test this, Cp_2TiCl was prepared by the reaction of Cp_2TiCl_2 with Zn powder in THF to give a green solution of the desired complex,[45] which upon addition to solutions of either **1a** or **1b** resulted in no reaction after 48 h. No reaction was also detected upon addition of $TiCl_3$ to a solution of **1a** or **1b** in toluene. The lack of reactivity showed that these Ti(III) complexes were inactive as precatalysts for the dehydrocoupling reaction.

4. Elucidation of the Homogeneous or Heterogeneous Nature of the Active Ti Catalyst. Due to the single site mode of reactivity of homogeneous catalysts, the identification of such a process might allow for the identification of reaction intermediates and elucidation of the reaction mechanism. It is therefore important to determine if the Ti(II) catalyst system operates in a homogeneous or heterogeneous manner. The previously described dehydrocoupling of **1a** using Rh(I) precatalysts such as $[Rh(\mu\text{-}Cl)(1,5\text{-}cod)]_2$ showed a sigmoidal-shaped kinetic profile that can be characteristic of a heterogeneous process, with an induction period prior to Rh colloid generation and a slow tailing off of the reaction rate associated with subsequent nanoparticle aggregation (red squares, Figure 3).[11,15] In contrast, the Ti(II) system $[Cp_2Ti]$ showed approximately linear consumption of **1a** (black circles, Figure 3). By comparison, reactions with $Cp_2Ti(PMe_3)_2$ showed a slight induction period, presumably due to dissociation of the phosphine ligands from the Ti(II) center,

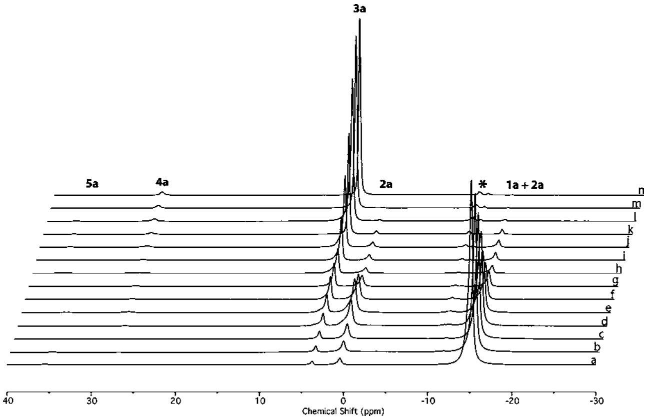


Figure 2. $^{11}B\{^1H\}$ NMR (96 MHz, unlocked, toluene) spectra showing conversion of **1a** (1.3 M in toluene) to **2a** and **3a** by $Cp_2Ti(PMe_3)_2$ as precatalyst (2 mol %, toluene, 20 °C), * = unidentified species. (a) $t = 9$ min, (b) $t = 15$ min, (c) $t = 19$ min, (d) $t = 29$ min, (e) $t = 46$ min, (f) $t = 60$ min, (g) $t = 106$ min, (h) $t = 162$ min, (i) $t = 179$ min, (j) $t = 213$ min, (k) $t = 245$ min, (l) $t = 300$ min, (m) $t = 364$ min, (n) $t = 439$ min.

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(43) Jegat, C.; Fouassier, M.; Tranquille, M.; Mascetti, J. *Inorg. Chem.* **1991**, *30*, 1529–1536.

(44) Attempts to recrystallise the microcrystalline product resulted in significant decomposition to unidentified species. Analysis of pure material (as assessed by ^1H, ^{13}C and ^{31}P NMR spectroscopy) by elemental analysis and mass spectrometery failed to provide useful and reproducible data.

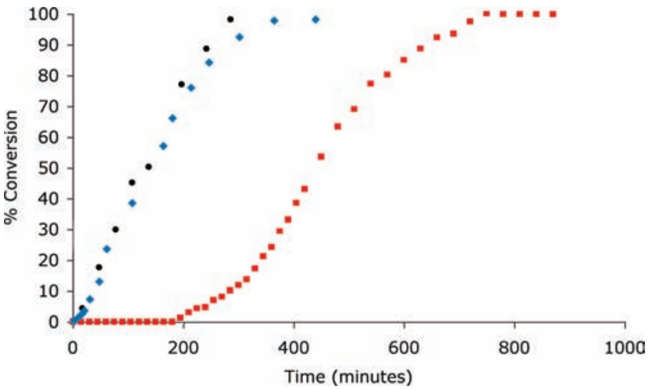

Figure 3. Graph of % conversion to **3a** vs time for the catalytic dehydrocoupling of **1a** using $[Rh(\mu\text{-}Cl)(1,5\text{-}cod)]_2$[11] (2 mol % Rh, toluene, 20 °C, red squares), $[Cp_2Ti]$ (2 mol % Ti, toluene, black circles) and $Cp_2Ti(PMe_3)_2$ (2 mol % Ti, toluene, blue diamonds).

followed by rapid catalytic consumption of **1a** to give **3a** (blue diamonds, Figure 3).[46]

Further insight was provided by experiments involving the addition of mercury to the catalytically active reaction mixtures. Mercury is a well-known poison of heterogeneous metal catalysts, owing either to its adsorption onto the catalyst surface or formation of an amalgam.[47] In contrast to the Rh-catalyzed dehydrocoupling of **1a**, which is completely halted by its addition,[11,15] the Ti-catalyzed reactions were unaffected even in the presence of a large excess (e.g., 71 equivalents) of the group 12 metal. A further indication that the latter is a homogeneous process was provided by nanofiltration experiments. These involved filtering the reaction mixture through a small pore (200 nm) membrane in order to distinguish between soluble and insoluble catalysts.[48] If the activity is dramatically lowered upon filtration, then an insoluble heterogeneous catalyst can be assumed. Significantly, filtration of the catalytically active $[Cp_2Ti]$ and $Cp_2Ti(PMe_3)_2$ solutions after 80 and 40 min reaction time respectively resulted in no detectable decrease in the rate of conversion of **1a** to **3a** (see Figure S6, Supporting Information, for data involving the $Cp_2Ti(PMe_3)_2$ precatalyst system). In analyzing these results, an important fact to consider is that any very small, colloidal Ti particles present in the reaction mixture would pass through the 200 nm filter and would, if catalytically active, result in a false positive test for a homogeneous catalyst. Notably however, both THF-soluble colloidal Ti, generated from $TiBr_4\cdot 2THF$ and $K[BEt_3H]$, in addition to bulk Ti powder, were found to be inactive for the catalytic dehydrocoupling of **1a** or **1b**. The results involving the kinetic profile, mercury poisoning and nanofiltration experiments therefore strongly support the presence of a homogeneous Ti catalyst.

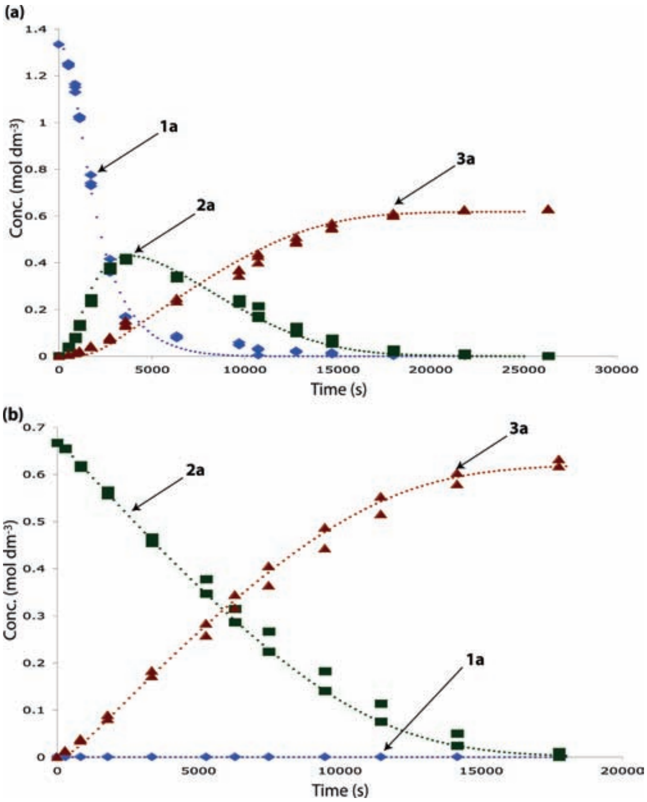

Figure 4. Graph showing conversion of (a) **1a** (1.3 M in toluene, blue diamonds) to **2a** (green squares) and **3a** (red triangles) by $Cp_2Ti(PMe_3)_2$ as precatalyst (0.027 M, 2 mol % in toluene) and (b) **2a** (0.67 M in toluene, green squares) to **3a** (red triangles) by $Cp_2Ti(PMe_3)_2$ (0.027 M, 4 mol % in toluene) (small dots (••••••) indicate data from kinetic model).

5. Kinetic and Mechanistic Studies for the $Cp_2Ti(PMe_3)_2$ Precatalyst System. As noted above, when the reaction of **1a** with $Cp_2Ti(PMe_3)_2$ was monitored by ^{11}B NMR spectroscopy, significant amounts of **2a** were detected at low conversion of the amine−borane adduct, followed by consumption to form **3a** (see Figure 2). It therefore appears likely that formation of **3a** occurs in two steps. Initially, the interaction of two equivalents of **1a** with $[Cp_2Ti]$ could result in the formation of a new B−N bond (to give **2a**), with the loss of one equivalent of H_2. Interaction of **2a** with the same active catalyst could then result in the loss of another equivalent of H_2, and the formation of another B−N bond to yield **3a**, along with trace amounts of **4a** and **5a** (Scheme 4). Because the results predicted by computational modeling[25] did not reflect the results observed for the catalytic dehydrocoupling of **1a** by $[Cp_2Ti]$ or $Cp_2Ti(PMe_3)_2$, we decided to carry out a preliminary mechanistic investigation.

Some insight into the reaction mechanism was obtained by monitoring reactions at different initial concentrations (**1a** = 2 M, $Cp_2Ti(PMe_3)_2$ = 0.040 M; **1a** = 0.67 M, $Cp_2Ti(PMe_3)_2$ = 0.015 M) and different precatalyst loadings (**1a** = 1.3 M, $Cp_2Ti(PMe_3)_2$ = 0.040 M; **1a** = 1.3 M, $Cp_2Ti(PMe_3)_2$ = 0.013 M). To ensure that the data obtained was of a suitable standard for a kinetic study, all reactions were repeated several times, with highly reproducible kinetics observed in every case (see overlay for three separate experiments in Figures 4 and S9−S12, Supporting Information). To investigate the conversion of **2a** to **3a** a sample of **2a** was synthesized by the literature method.[15] Addition of a catalytic amount of $Cp_2Ti(PMe_3)_2$ (0.027 M in toluene) to a solution of **2a** (0.67 M in toluene) resulted in

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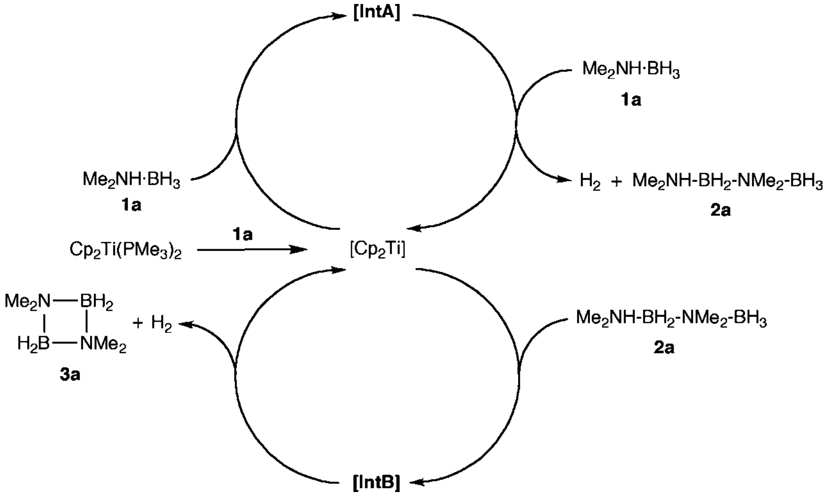
(45) Rajanbabu, T. V.; Nugent, W. A. *J. Am. Chem. Soc.* **1994**, *116*, 986–997.

(46) As the dehydrocoupling reactions of **1a** by both $[Cp_2Ti]$ and $Cp_2Ti(PMe_3)_2$ occur at very similar rates (after the brief induction period in the latter case) the presence of phosphine in the reaction mixture appears to have a negligible impact on the reaction at the concentrations in our experiments.

(47) (a) Whitesides, G. M.; Hackett, M.; Brainard, R. L.; Lavalleye, J. P. P. M.; Sowinski, A. F.; Izumi, A. N.; Moore, S. S.; Brown, D. W.; Staudt, E. M. *Organometallics* **1985**, *4*, 1819–1830. (b) Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855–859.

(48) Widegren, J. A.; Finke, R. G. *J. Mol. Catal. A: Chem.* **2003**, *198*, 317–341.

Scheme 9. Catalytic Cycle Employed to Model the Kinetics of the [Cp_2Ti] Catalyzed Dehydrocoupling of **1a**



complete conversion to **3a** in 5 h (Figures 4b and S8a, Supporting Information). It is significant to note that the reaction of preformed **2a** with $Cp_2Ti(PMe_3)_2$ did not result in the reformation of **1a** or significant amounts of **4a** (2.5%) and **5a** (0.5%), strongly indicating that **2a** is indeed the sole precursor to **3a**.

Although full analytical rate equations can be derived for catalytic systems, for example using the method of King and Altman,[49] the complex nature of the reaction networks involved can make it challenging to simplify the rate equation through the application of limiting conditions. In such cases, computational modeling can be used to efficiently test various mechanistic hypotheses, through the numerical fitting of simple models to the data.[50] By applying a two-cycle model to our experimental data, each involving two steps, it was possible to achieve a reasonable fit (Scheme 9 and Figures 4 and S7−S12, Supporting Information).

In this simple model, the precatalyst $Cp_2Ti(PMe_3)_2$ is activated[51] by **1a** to form active species [Cp_2Ti], which then interacts with a molecule of **1a** to form the intermediate **[IntA]**. Addition of a further equivalent of **1a** to **[IntA]** results in loss of both H_2 and **2a** from the metal center and regeneration of [Cp_2Ti]. The interaction of **2a** with the same active catalyst, [Cp_2Ti], then results in the generation of intermediate **[IntB]**, from which **3a** and a second equivalent of H_2 are lost, also regenerating [Cp_2Ti]. The resting states of the system are **[IntA]** and **[IntB]**, resulting in an approximate pseudo zero-order consumption of **2a** and evolution of **3a**. Importantly, the same model satisfactorily predicted the kinetics of the independent conversion of **2a** to **3a** (Figures 4b and S18, Supporting Information).

The observation of kinetic isotope effects can yield important information pertaining to reaction mechanisms. We therefore explored the kinetic isotope effects associated with the dehydrocoupling of **1a**. The synthesis of deuterated **1a** was achieved by the reaction of Me_2NH with $BD_3 \cdot THF$ yielding $Me_2NH \cdot BD_3$ (**1aBD**) (74% yield), exchange of the protic hydrogen of **1a** or **1aBD** in D_2O, yielding $Me_2ND \cdot BH_3$ (**1aND**) (82% yield) and $Me_2ND \cdot BD_3$ (**1aNDBD**) (84% yield), respectively (Scheme 10).

Scheme 10. Synthesis of Deuterated Dimethylamine−Borane Adducts **1aND**, **1aBD** and **1aNDBD**

$$Me_2NH \cdot BH_3 \xrightarrow{D_2O} Me_2ND \cdot BH_3 \quad \textbf{(1aND)}$$

$$Me_2NH + BD_3 \cdot THF \xrightarrow[-75°C]{THF} Me_2NH \cdot BD_3 \quad \textbf{(1aBD)}$$

$$Me_2NH \cdot BD_3 \xrightarrow{D_2O} Me_2ND \cdot BD_3 \quad \textbf{(1aNDBD)}$$

We performed the catalytic dehydrocoupling of the deuterated amine−borane adducts **1aND**, **1aBD** and **1aNDBD** with $Cp_2Ti(PMe_3)_2$ and observed by ^{11}B NMR spectroscopy the initial formation of linear dimer, and subsequent conversion to cyclic dimer, as with the nondeuterated adduct **1a**. Reactions reached 100% conversion to cyclic dimer **3a** in 32 h, 9 and 33 h for **1aND**, **1aBD** and **1aNDBD,** respectively (compared to 7 h for **1a** under similar conditions) (see Figures S7 and S13−S15, Supporting Information).

Due to oversimplifications necessary in the derivation of the kinetic model, this data could not be used to extract kinetic isotope effects pertinent to individual steps. Instead, the pseudo zero-order phases of consumption of **1a** and evolution of **3a**, were employed to extract phenomenological k_H/k_D values of 3.6 ± 0.3 for N−H/D, 1.7 ± 0.3 for B−H/D and 4.5 ± 0.3 for B−H/D + N−H/D in the conversion of **1a** to **2a**, and 4.7 ± 0.3 for N−H/D, 1.4 ± 0.2 for B−H/D and 5.3 ± 0.3 for B−H/D + N−H/D in the conversion of **2a** to **3a** (Figures S16−S17, Supporting Information).

The low k_H/k_D values associated with B−H/D cleavage in both steps (**1a** to **2a** and **2a** to **3a**) may arise from small transfer angles, exceptionally early or late transition states or B−H/D cleavage outside of the turnover limiting step.[52] However, due to the limitations of the ^{11}B NMR spectroscopic method employed we did not conduct competition experiments to probe for the latter.[53]

Discussion

The involvement of linear dimer **2a** in the dehydrocoupling of **1a** has been previously suggested for [$Rh(\mu\text{-}Cl)(1,5\text{-}cod)]_2$[15]

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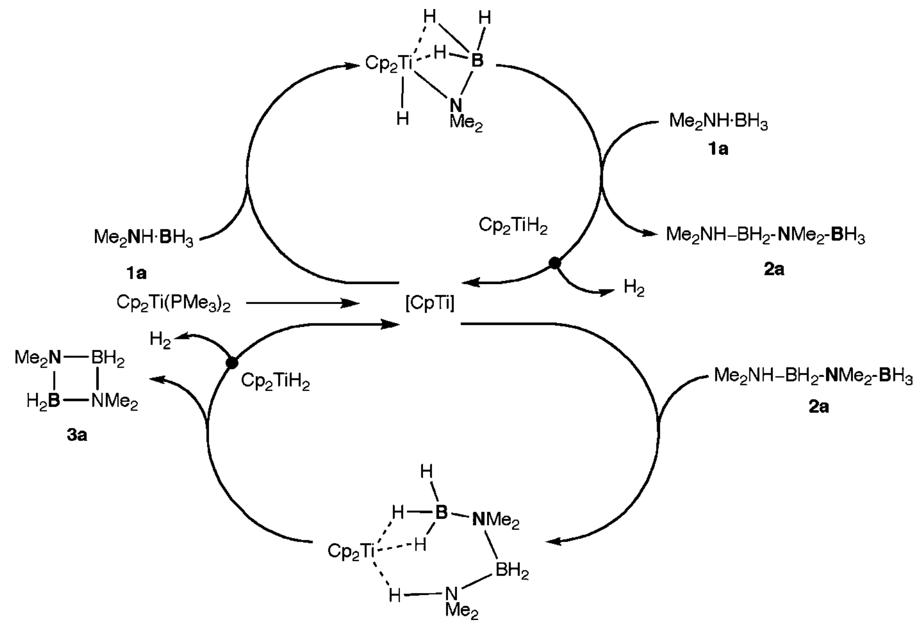
(49) King, E. L.; Altman, C. *J. Phys. Chem.* **1956**, *60*, 1375–1378.

(50) (a) Stabler, R. N.; Chesick, J. P. *Int. J. Kinet.* **1978**, *10*, 461–469. (b) Weigert, F. *J. Comput. Chem.* **1987**, *11*, 273–280.

(51) Comparison of initial rates of consumption of **1a** and **2a** by $Cp_2Ti(PMe_3)_2$ indicated a difference in the induction period. Whilst a dissociative mechanism for the loss of the first PMe_3 ligand from the precatalyst seems reasonable, loss of the second ligand, and thus generation of the active catalyst, may be influenced differently by **1a** and **1b**.

(52) O'Ferrall, R. A. *J. Chem. Soc. B.* **1970**, 785–790.

Scheme 11. Summary of Catalytic Cycle with Proposed Intermediates



as precatalyst and also very recently for cationic Rh-[18] and neutral Ru-based[7] systems. However, previous computational work by Ohno and Luo discounted the formation of **2a** during the catalytic dehydrocoupling of **1a** by [Cp$_2$Ti].[25] Their calculations implied that **3a** was formed via an intramolecular, stepwise mechanism (exergonic by 7.4 kcal/mol), where **5a** is formed during the interaction of **1a** with [Cp$_2$Ti] and then undergoes an uncatalyzed dimerization cyclization reaction to form **3a** (Scheme 3). These workers also investigated the possibility of an intermolecular mechanism (**1a** → **2a** → **3a**), but eventually ruled it out for kinetic and thermodynamic reasons; the transition state barrier for [Cp$_2$Ti]-catalyzed transformation of **1a** to **2a** was calculated to be + 37.2 kcal/mol and the reaction to be endergonic by 4.1 kcal/mol.[25] As a result, they did not calculate a route to the catalytic ring closing dehydrocoupling of **2a** to yield **3a**. It is therefore significant to experimentally observe that **2a** is both generated and catalytically converted to **3a**, rather than **3a** being generated by the cycloaddition of 2 molecules of **5a**,[54] and that in the absence of catalyst, **2a** is stable. This demonstrates that the reaction mechanism is different than that proposed by Luo and Ohno (Scheme 3).

Regarding the overall mechanism, in Scheme 11 we propose a two cycle mechanism with plausible proposed structures for intermediates. We propose that **1a** initially coordinates to [Cp$_2$Ti] via a 3-center-2-electron Ti−H−B interaction to give [Cp$_2$Ti(η^2-BH$_3$·NHMe$_2$)]. Complexes of this type have been characterized for late transition metals. For example, the involvement of the late transition metal complex [Rh(P^{i}Bu$_3$)$_2$-(η^2-H$_3$B·NHMe$_2$)][BAr$^F{}_4$] in the catalytic dehydrocoupling of **1a** has been discussed by Weller and co-workers.[9] Interaction of the protic hydrogen with the Ti(II) center would then result in proton transfer and formation of intermediate [**IntA**], [Cp$_2$Ti(H)NMe$_2$·BH$_3$]. The primary KIE of 3.6 ± 0.3 may be associated with this step; the magnitude of the effect being similar to that observed in other transition metal mediated N−H cleavage reactions.[55] A reaction mechanism of this type was proposed by Ohno and Luo as the first step in the intramolecular stepwise catalytic dehydrocoupling of **1a** (Scheme 3). A range of similar titanium amido−borane complexes have previously been reported by Lancaster and co-workers,[56] while analogous zirconocene hydrido amido−borane complexes [Cp$_2$Zr(H)NH$_2$·BH$_3$] have recently been reported by Roesler and co-workers.[57] The second step would involve the approach of a second molecule of **1a** to [**IntA**] and formation of a new B−N bond between the two adducts at the metal center, followed by dissociation of **2a** and loss of H$_2$ from the Ti center and reformation of the catalytically active species [Cp$_2$Ti].

Conversion of **2a** to **3a** could then proceed via a similar route to the formation of **2a**, with precoordination of **2a** to the Ti-center through a 3-center-2-electron Ti−H−B interaction at the BH$_3$ terminus, followed by interaction of Ti with the N−H bond, forming intermediate [**IntB**], [Cp$_2$Ti(η^2-BH$_3$−NMe$_2$BH$_2$NH-Me$_2$]. Similar complexes have been reported for the later transition metals by Weller and co-workers, for example [Rh(P^{i}Bu$_3$)$_2$(η^2-H$_3$B·NMe$_2$BH$_2$·NHMe$_2$)][BAr$^F{}_4$],[18] while Shimoi and co-workers have reported the *in situ* identification of a η^1-bound early transition metal complex of **2a**, [Cr(CO)$_5$(η^1-BH$_3$−NMe$_2$-BH$_2$−NHMe$_2$)].[21] Such species could then undergo a Ti/N−H insertion reaction to yield **3a** (Scheme 11).

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(53) Due to overlap of the signals corresponding to deuterated and non-deuterated adducts **1a**, **1aND**, **1aBD** and **1aNDBD**, analysis of the corresponding ^{11}B or ^{1}H NMR signals could not provide information regarding the outcome of a competition reaction.

(54) Analysis of the reaction mixture by ^{11}B NMR spectroscopy identified small amounts of **5a**, which remained constant throughout the reaction, and were still present after full consumption of **1a**. It is therefore clear that in this reaction **3a** is not mainly formed by the cycloaddition of two molecules of **5a**; however, we cannot discount this reaction playing a role as a minor pathway.

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Our mechanistic proposals for the [Cp_2Ti] system are interesting to compare with those of other groups for related early and also late transition metal catalysts. As noted above, the computational results of Luo and Ohno[25] for the [Cp_2Ti]-catalyzed dehydrogenation of **1a** appear inconsistent with our results, which point to a key role for the linear dimer **2a**. Chirik and co-workers have also studied the use of group 4 metallocene complexes for the catalytic dehydrogenation of amine−borane adducts.[26] Based on reactions performed under an atmosphere of D_2 and first order rate constants for **1a** as a substrate and the highly active Ti(II) dinitrogen complex [$\{(1,3\text{-}(SiMe_3)_2C_5H_3)_2Ti\}_2(\eta^1\text{-}N_2)$] as a precatalyst, these workers suggested that the reaction proceeds initially via reversible B−H oxidative addition to form a Ti−boryl complex. Subsequent, reversible β-hydride elimination to generate **5a**, which then dimerizes to the cyclic dimer **3a**, was then proposed. This mechanism, which also does not postulate a role for **2a**, is similar to that previously proposed for amineborane dehydrogenation by Ni[6] and more recently Re catalysts.[20] In the case of Cr carbonyl[21] and Ir pincer complexes[5,19] as catalysts, the formation of linear dimers has also not been noted and, in these cases, a mechanism that involves concerted removal of H_2 from the substrate has been proposed.[59]

Recently, other workers have also reported intriguing studies of the catalytic dehydrogenation of **1a** by late transition metal complexes where the linear dimer **2a** has been detected as an intermediate.[60] For example, Weller, Hall and co-workers have proposed that catalysis by the cationic Rh(I) complexes [$Rh(PR_3)_2$][BAr^f_4] proceeds via sequential B−H/N−H activation and transfer steps followed by sequential loss of H_2 and **5a**. In this case, although linear dimer **2a** was detected in reaction mixtures, the mechanistic role of this species was unclear. Moreover, conversion of **2a** to **3a** was not found to occur via a simple intramolecular route.[18] In another study, Schneider and co-workers have also investigated the dehydrocoupling of **1a** by a Ru amido pincer complex and identified the linear dimer **2a** as an important intermediate.[7] These workers suggest that linear **2a** and **5a** are formed from **1a** via competitive pathways. Interestingly, in this case, conversion of **2a** to **3a** appears to take place via a combination of pathways that involve direct metal-catalyzed dehydrogenative cyclization and B−N bond scission to afford **5a**, which subsequently dimerizes. In our study with [Cp_2Ti] as the catalyst, the former pathway appears to be dominant for the formation of **3a**. Nevertheless, work by Zimmerman and co-workers[61] has highlighted the possible autocatalytic role of $NH_2{=}BH_2$, which leads to H_2 loss and oligomerization of **1e**, without the need for a transition metal catalyst. In considering an analogous possibility for **1a** we were able to exclude such autocatalytic pathways by observing that isolating a mixture of products **2a**, **3a**, **4a**, and **5a** and starting material **1a** from the catalyst resulted in no further conversion of **1a** to **3a**, and only slow decay of the signal corresponding to **5a** (Figure S19 and S20, Supporting Information).[62]

Summary

We have demonstrated the efficient homogeneous catalytic dehydrocoupling of the secondary amine−borane adduct **1a** by the putative early transition metal complex [Cp_2Ti], generated *in situ* by the reaction of Cp_2TiCl_2 and 2^{n}BuLi or from the isolable precatalyst $Cp_2Ti(PMe_3)_2$. Catalytic screening of a series of group 4 complexes has highlighted the decreased activity on descending the group and on substitution of the cyclopentadienyl ligands by bulky or electron donating groups. The lack of reactivity of the secondary amine−borane adducts **1a** and **1b** with either Ti(III) or Ti(0) species supports the presence of a catalytically active Ti(II) complex. In contrast to the case with Rh(I) precatalysts, the electron rich and sterically encumbered amine−borane adduct **1b** shows enhanced reactivity, suggesting that in the case of the early transition metal catalyst the electronic and/or steric nature of the adduct has an opposite effect on the reaction rate. Kinetic analysis of the conversion of **1a** to **3a** with $Cp_2Ti(PMe_3)_2$ as a precatalyst indicates a two stage catalytic reaction mechanism, with initial formation of linear species **2a**, which undergoes a catalytic ring-closing dehydrocoupling process to afford cyclic species **3a**. These experimental results contrast with theoretical predictions[25] that suggested monomeric species **5a** is formed catalytically, and then undergoes an uncatalysed 2 + 2 cycloaddition reaction to form **3a**.

Experimental Section

General Procedures and Materials. All reactions and manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques or in a MBraun glovebox filled with dry argon. NMR experiments were carried out on Jeol ECP 300 MHz (^{31}P, ^{11}B, ^{1}H, ^{2}H), Jeol Lambda 300 MHz (^{31}P, ^{1}H) or Varian VNMR 400 MHz (^{1}H, ^{13}C) spectrometers. Spectra were internally referenced to residual solvent peaks (^{1}H, ^{2}H, ^{13}C) or externally referenced to $BF_3\cdot Et_2O$ (^{11}B) or H_3PO_4 (^{31}P). Tetrahydrofuran was distilled from Na/benzophenone. Diethyl ether, toluene and hexanes were purified using a Grubbs solvent system. Mercury (99.9995%), Ti powder (100 mesh), $TiCl_3$, $TiCl_4$, Me_2NH (2 M solution in THF), $MeNH_2$ (gas), PMe_3 and ^nBuLi (1.6 M solution in hexanes) and Millex Millipore filters (PTFE membrane, 0.2 μm pore size) were purchased from Aldrich, Cp_2TiCl_2 (98%) was purchased from Acros, Zn powder was purchased from BDH laboratories, Na was purchased from Fisher Scientific, Cp_2HfCl_2 was purchased from Strem and Cp_2ZrCl_2 was purchased from Fluka, all used as received. $BD_3\cdot THF$ (1 M THF) was purchased from Cambridge Isotope Laboratories and was used as received. D_2O was purchased from Fluorochem and was degassed (3 × freeze−pump−thaw cycles) prior to use. $BH_3\cdot THF$ (1 M THF) was purchased from Acros and distilled under a static vacuum prior to use. $Me_2NH\cdot BH_3$ (97%) was purchased from Aldrich and further purified by vacuum sublimation twice at 20 °C. $^iPr_2NH$ and MeBnNH were purchased from Aldrich and were vacuum distilled from CaH_2. Cp_2TiCl,[45] $Me_2Si(\eta^5\text{-}C_5H_4)_2MCl_2$ where M = Ti or Zr,[42] $Cp_2Ti(PMe_3)_2$,[43] $(\eta^5\text{-}C_5Me_4SiMe_2{}^tBu)_2Ti$,[30] $Ph_2PH\cdot BH_3$,[12] $(p\text{-}CF_3C_6H_4)PH_2\cdot BH_3$,[13] $R'RNH\cdot BH_3$ ($R' = R = {}^iPr$; $R' = Bn$, $R = Me$; $R' = Me$, $R = H$),[15] $Me_2NH\text{-}BH_2\text{−}NMe_2\text{-}BH_3$[15] and THF soluble Ti colloids[58] were synthesized following literature procedures. All reactions were repeated at least twice with reproducible yields.

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(60) During the analogous treatment of **1c** with [Cp_2Ti] ^{11}B NMR signals assigned to linear dimer MeBnNH-BH_2−MeBnN-BH_3 were also detected. The linear dimer was then found to decrease in concentration as cyclic dimer **3c** was formed. In the case of **1b** no intermediates were detected by ^{11}B NMR spectroscopy in the conversion to **5b**.

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(62) See experimental for details. The compound $H_2B(\mu\text{-}NMe_2)(\mu\text{-}H)BH_2$ was also formed during isolation of the reactant and products from the catalyst.

Catalytic Dehydrocoupling of $Me_2NH\cdot BH_3$ (1a), $^iPr_2NH\cdot BH_3$ (1b), $MeBnNH\cdot BH_3$ (1c) or $MeNH_2\cdot BH_3$ (1d) by Cp_2TiCl_2/2^{n}BuLi. To a solution of Cp_2TiCl_2 (0.020 g, 0.080 mmol) in toluene (2 mL), ^{n}BuLi (0.10 mL, 0.160 mmol) was added at −15 °C giving an amber solution. After 5 min, the reaction mixture was removed from the cooling bath and to this solution, **1a** (0.24 g, 4.1 mmol), **1b** (0.46 g, 4.0 mmol), **1c** (0.54 g, 4.0 mmol) or **1d** (0.18 g, 4.0 mmol) in toluene (1 mL) was added resulting in a color change to black and gas evolution in the cases of **1a**, **1b** and **1c**. An aliquot was then removed and analyzed by ^{11}B NMR spectroscopy, indicating complete conversion to products **3a** ^{11}B NMR δ 4.8 (t, $^1J_{B-H}$ = 112 Hz), **5b** ^{11}B NMR δ 34.7 (t, $^1J_{B-H}$ = 127 Hz) and **3c** ^{11}B NMR δ 3.9 (t, $^1J_{B-H}$ = 99 Hz) after 4 h, 1 and 1.5 h respectively.

Control Reaction of 1a with ^{n}BuLi. To a solution of **1a** (0.051 g, 0.87 mmol) in toluene (2 mL), ^{n}BuLi (0.050 mL, 0.08 mmol) was added at −10 °C with no observable change. The reaction mixture was allowed to warm to 20 °C and stirred for 16 h. After this time, an aliquot of the reaction mixture was removed and the ^{11}B NMR spectrum obtained, showing a single signal corresponding to unreacted **1a**.

Catalytic Dehydrocoupling of 1a. Mercury Poisoning Experiment. A typical dehydrocoupling trial with [Cp_2Ti] (from systems Cp_2TiCl_2/2^{n}BuLi or $Cp_2Ti(PMe_3)_2$) was allowed to proceed with monitoring by ^{11}B NMR spectroscopy for 80 min. After this time the reaction mixture was transferred to a flask containing Hg (71 equiv) and stirred vigorously. IMPORTANT. Good stirring is necessary to ensure contact of the catalyst with Hg(0), a condition required to avoid false negatives in this experiment. Periodic monitoring was performed by ^{11}B NMR spectroscopy, which showed complete conversion to **3a** after 4 and 7 h, for the precatalyst systems Cp_2TiCl_2/2^{n}BuLi and $Cp_2Ti(PMe_3)_2$ respectively.

Catalytic Dehydrocoupling of 1a. Filtration Experiment. A typical dehydrocoupling trial with [Cp_2Ti] (from systems Cp_2TiCl_2/2^{n}BuLi or $Cp_2Ti(PMe_3)_2$) was allowed to proceed with monitoring by ^{11}B NMR spectroscopy for 80 min. After this time, the mixture was filtered through a 0.2 μm filter into a new flask with a new stir bar and the reaction continued with monitoring by ^{11}B NMR spectroscopy showing full conversion to **3a** after 4 and 7 h for the precatalyst systems Cp_2TiCl_2/2^{n}BuLi and $Cp_2Ti(PMe_3)_2$ respectively.

Attempted Reaction of 1a with Colloidal Ti Metal. To a solution of **1a** (0.20 g, 3.4 mmol) in toluene (2 mL), Ti (0.016 g, 0.33 mmol) in THF (1 mL) was added at 20 °C with no observable change. The reaction mixture was allowed to stir for 16 h. After this time, an aliquot of the reaction mixture was removed and the ^{11}B NMR spectrum showed a single signal corresponding to unreacted **1a**.

Attempted Reaction of 1a with Ti Powder. To a solution of **1a** (0.20 g, 3.4 mmol) in toluene (3 mL) Ti powder (16.0 mg, 100 mesh) was added, and the mixture was stirred for 20 h. Analysis of an aliquot by ^{11}B NMR spectroscopy showed only unreacted starting material **1a**.

Attempted Catalytic Dehydrocoupling of 1e by [Cp_2Ti]. To a solution of [Cp_2Ti], generated in the usual manner, a slurry of **1e** (0.13 g, 4.1 mmol) in diglyme (5 mL) was added resulting in a color change to gray. After stirring at 20 or 45 °C for 16 h, a small amount of solution was removed from the reaction mixture and the ^{11}B NMR spectrum obtained which showed a single signal corresponding to unreacted **1e**.

Attempted Catalytic Dehydrocoupling of $Ph_2PH\cdot BH_3$ by [Cp_2Ti]. To a solution of [Cp_2Ti], generated in the usual manner, a solution of $Ph_2PH\cdot BH_3$ (0.19 g, 0.95 mmol) in toluene (1 mL) was added resulting in a color change to blue-black. After stirring at 20 or 40 °C for 16 h, a small amount of solution was removed from the reaction mixture and the ^{11}B and ^{31}P NMR spectra were obtained, which showed single signals (^{11}B δ −41.0, ^{31}P δ 1.97) in each case corresponding to unreacted $Ph_2PH\cdot BH_3$.[12]

Attempted Catalytic Dehydrocoupling of (p-$CF_3C_6H_4$)$PH_2\cdot BH_3$ by [Cp_2Ti]. To a solution of [Cp_2Ti], generated in the usual manner, a solution of (p-$CF_3C_6H_4$)$PH_2\cdot BH_3$ (0.31 g, 1.6 mmol) in toluene (1 mL) was added, resulting in a color change to dark green. After stirring at 20 or 40 °C for 16 h, a small amount of solution was removed from the reaction mixture and the ^{11}B and ^{31}P NMR spectra were obtained, showing single signals (^{11}B δ −33.6, ^{31}P δ −48.3) in both cases corresponding to unreacted (p-$CF_3C_6H_4$)$PH_2\cdot BH_3$.[13]

Attempted Dehydrocoupling of 1a and 1b with [Cp_2Zr]. To a solution of Cp_2ZrCl_2 (0.025 g, 0.085 mmol) in THF (2 mL), ^{n}BuLi (0.10 mL, 0.17 mmol) was added at −15 °C to give a light-green solution which was stirred for 5 min and then allowed to warm to 20 °C for 5 min. A solution of **1a** (0.10 g, 1.7 mmol) or **1b** (0.20 g, 1.74 mmol) in THF (1 mL) was added and the solution stirred for 20 h after an aliquot was removed for analysis by ^{11}B NMR spectroscopy.

Attempted Dehydrocoupling of 1a and 1b with [Cp_2Hf]. To a solution of Cp_2HfCl_2 (0.064 g, 0.16 mmol) in THF or toluene (2 mL), ^{n}BuLi (0.21 mL, 0.34 mmol) was added at −15 °C to give a colorless solution which was stirred for 5 min and then allowed to warm to 20 °C for 5 min. A solution of **1a** (0.20 g, 3.5 mmol) or **1b** (0.37 g, 3.2 mmol) in THF or toluene (1 mL) was added and the solution stirred for 20 h, after which analysis of an aliquot by ^{11}B NMR spectroscopy indicated only starting material for **1a** and product **5b** when either THF or toluene was used.

Attempted Catalytic Dehydrocoupling of 1a or 1b with Cp_2TiCl. To a solution of Cp_2TiCl_2 (0.0050 g, 0.020 mmol) in THF (2 mL) Zn powder (0.0050 g, 0.076 mmol) was added and the resulting mixture stirred for 30 min, resulting in a bright green solution. To this a solution of **1a** (0.25 g, 4.2 mmol) or **1b** (0.36 g, 3.1 mmol) in THF (1 mL) was added. The reaction mixture was allowed to stir for 20 h. After this time, an aliquot of the reaction mixture was removed and the ^{11}B NMR spectrum obtained which showed a single signal corresponding to unreacted **1a** or **1b**, respectively.

Attempted Catalytic Dehydrocoupling of 1a or 1b with $TiCl_3$. To a solution of **1a** (0.25 g, 4.2 mmol) or **1b** (0.36 g, 3.1 mmol) in toluene (3 mL), $TiCl_3$ (0.013 g, 0.084 mmol) was added at 20 °C giving a purple slurry. The reaction mixture was allowed to stir for 20 h. After this time, an aliquot of the reaction mixture was removed and the ^{11}B NMR spectrum obtained showing a single signal corresponding to unreacted **1a** and **1b**, respectively.

Synthesis of $Cp_2Ti(PMe_3)_2$. Repeated attempts to synthesize $Cp_2Ti(PMe_3)_2$ by established methods failed to achieve pure material.[43] A suspension of Cp_2TiCl_2 (2.0 g, 8.0 mmol) in a solution of PMe_3 (4.0 mL, 39 mmol) in Et_2O (80 mL) was slowly added to Na/Hg (100 g, 1 wt %), and the resulting mixture stirred for 12 h. The resulting dark-red/brown solution was filtered through Celite, and the volatiles removed under a strong flow of argon giving 1.76 g (66% yield) of the dark-red/black crystalline solid $Cp_2Ti(PMe_3)_2$. Attempted recrystallization resulted in partial decomposition of the product and a reduction in purity. ^{1}H NMR (C_6D_6, 400 MHz) δ 4.57 (s, 10H), 0.84 (s, 18H), ^{13}C NMR (C_6D_6, 100 MHz) δ 90.1 (s, 2 × Cp), 22.5 (s, 6 × Me), ^{31}P NMR (C_6D_6, 121 MHz) δ 40.6 (s).

Synthesis of $Me_2ND\cdot BH_3$ (1aND). $Me_2NH\cdot BH_3$ (10.0 g, 0.17 mol) was dissolved in degassed D_2O (30 mL, 1.7 mols) and stirred at 40 °C for 24 h. The solution was then extracted with CH_2Cl_2 (3 × 100 mL), the organic layer was dried with $MgSO_4$ and filtered, and the volatiles were removed. The resulting solid was sublimed twice under dynamic vacuum at 20 °C to give 8.21 g (82% yield) of **1aND**. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.5 (s, 6H), 1.5 (q, $^1J_{BH}$ = 92 Hz, 3H), ^{2}H NMR ($CHCl_3$, 46 MHz) δ 3.8 (br), ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.6 (s), ^{11}B NMR (96 MHz, $CDCl_3$) δ −14.1 (q, $^1J_{BH}$ = 92 Hz).

Synthesis of $Me_2NH\cdot BD_3$ (1aBD). Me_2NH (28 mL, 55.0 mmol, 2 M in THF) was added to a solution of $BD_3\cdot THF$ (50 mL, 50.0 mmol, 1 M in THF) in THF (100 mL) at −75 °C, and the solution allowed to warm slowly to 20 °C. Removal of the volatiles gave a colorless solid which was sublimed under dynamic vacuum twice at 20 °C to give 2.3 g (74% yield) of **1aBD**. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.1 (br, 1H), 2.5 (s, 6H), ^{2}H NMR ($CHCl_3$, 46 MHz) δ

2.9 (q, br., ${}^1J_{\mathrm{BD}} = 14.2$ Hz), ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.5 (s), ^{11}B NMR (96 MHz, $CDCl_3$) δ −14.1 (septet, ${}^1J_{\mathrm{BD}} = 14.2$ Hz).

Synthesis of $Me_2ND\cdot BD_3$ (1aNDBD). $Me_2NH\cdot BD_3$ (1.1 g, 17.0 mmol) was dissolved in degassed D_2O (7 mL, 0.39 mol) at 40 °C and stirred for 24 h. The solution was then extracted with CH_2Cl_2 (3 × 100 mL), the organic layer was dried with $MgSO_4$ and filtered, and the volatiles were removed. The resulting solid was sublimed twice under dynamic vacuum to give 0.895 g (84% yield) of **1aNDBD**. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.5 (s, 6H), ^{2}H NMR ($CHCl_3$, 46 MHz) δ 4.1 (s br), 2.9 (q, br., ${}^1J_{\mathrm{BD}} = 14.1$ Hz), ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.6 (s), ^{11}B NMR ($CDCl_3$, 96 MHz) δ −14.0 (sept, ${}^1J_{\mathrm{BD}} = 14.1$ Hz).

General Method for Kinetic Monitoring of Dehydrocoupling of 1a or 2a by $Cp_2Ti(PMe_3)_2$. To a solution of $Me_2N(H/D)\cdot B(H/D)_3$ (8 mmol) or **2a** (4 mmol) in toluene (4 mL) $Cp_2Ti(PMe_3)_2$ (2 mol % or 4 mol % for **1a** and **2a** respectively) in toluene (2 mL) was added, and the resulting mixture was monitored by ^{11}B NMR spectroscopy at regular time intervals until 100% conversion to **3a** was achieved.

Reaction conditions were varied in **1a** concentration (0.67, 1.3, and 2.0 M) at constant precatalyst loading. Precatalyst loading was varied (1, 2, and 3 mol %) for **1a**, and adduct choice ($Me_2NH\cdot BH_3$, $Me_2ND\cdot BH_3$, $Me_2NH\cdot BD_3$ or $Me_2ND\cdot BD_3$).

Isolation of Reactants and Products from Catalyst. To a solution of Cp_2TiCl_2 (0.020 g, 0.080 mmol) in toluene (2 mL), ^{n}BuLi (0.10 mL, 0.160 mmol) was added at −15 °C giving an amber solution. After 5 min, the reaction mixture was removed from the cooling bath, warmed to room temperature, and to this solution, **1a** (0.24 g, 4.1 mmol) in toluene (1 mL) was added resulting in a color change to black and gas evolution. After 50 min reaction time the reaction mixture was cooled to −78 °C and a distillation bridge and receiver flask attached. The volatile contents of the reaction were vacuum transferred to the receiver flask, with heating. Analysis by ^{11}B NMR, showed a mixture of **1a** (∼ 1.4%), **2a** (∼22.4%), **3a** (∼66.5%), **4a** (∼4.3%), **5a** (∼0.7%) and (μ-NMe_2)B_2H_5 (∼4.7%) (^{11}B NMR (96 MHz, toluene unlocked) δ −18.3 (dt, ${}^1J_{\mathrm{BHt}} = 129$ Hz, ${}^1J_{\mathrm{BHb}} = 30$ Hz) (lit. δ −17.0 (dt, ${}^1J_{\mathrm{BHt}} = 130$ Hz, ${}^1J_{\mathrm{BHb}} = 30$ Hz)[63]) After 24 h reexamination of the mixture by ^{11}B NMR spectroscopy showed the same product distribution except for the amount of **5a** which had decreased to ∼0.2% (Figure S19 and S20, Supporting Information).

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Supporting Information Available: Relevant NMR spectra and kinetic plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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