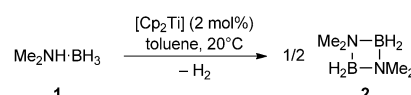


# Paramagnetic Titanium(III) and Zirconium(III) Metallocene Complexes as Precatalysts for the Dehydrocoupling/Dehydrogenation of Amine–Boranes\*\*

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Catalytic dehydrocoupling/dehydrogenation of amine–borane adducts has become a field of rapid growth over the past decade.<sup>[1]</sup> This development has been driven by potential applications with respect to hydrogen storage,<sup>[1,2]</sup> transfer hydrogenations and reductions of organic substrates,<sup>[3]</sup> and the preparation of new inorganic polymeric and solid-state materials.<sup>[4,5]</sup> A wide variety of catalyst systems have been developed that promote this reaction,<sup>[6–10]</sup> most of which are based on complexes of second- and third-row late transition metals. Mechanistic interest in these transformations has also led to the emergence of an interesting new area of coordination chemistry associated with amine–borane and amino–borane ligands.<sup>[11–13]</sup> Although much less developed, the catalytic dehydrogenation of phosphine–boranes appears to offer similar potential.<sup>[14]</sup>

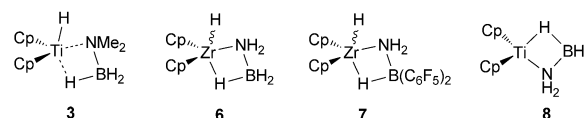
We have previously reported that the first-row Group 4 metallocene  $[\text{Cp}_2\text{Ti}]$ , generated in situ from  $[\text{Cp}_2\text{TiCl}_2]$  and  $n\text{BuLi}$  (2 equiv) or, alternatively, from the isolable  $\text{Ti}^{\text{II}}$  precatalyst  $[\text{Cp}_2\text{Ti}(\text{PMe}_3)_2]$ , functions as an efficient homogeneous catalyst for the dehydrogenation of secondary amine–borane adduct **1** to give the cyclodiborazane **2** (Scheme 1).<sup>[7]</sup> Chirik<sup>[8]</sup> and, more recently, Rosenthal<sup>[9]</sup> and co-workers have described analogous studies of a series of active  $\text{Ti}^{\text{II}}$  and  $\text{Zr}^{\text{II}}$  precatalysts for the dehydrocoupling of **1**. In general, the  $\text{Ti}$ -



**Scheme 1.** Titanocene-catalyzed dehydrogenation of **1**.

based precatalysts studied to date were found to be far more active than their  $\text{Zr}$ -based congeners.

Mechanistic proposals for the titanocene-catalyzed dehydrogenation of **1** have differed in many key details, but in all cases, diamagnetic  $\text{Ti}^{\text{II}}$  or  $\text{Ti}^{\text{IV}}$  precatalysts and intermediates have been invoked. For example, based on DFT calculations, Luo and Ohno suggested that interaction of **1** with  $[\text{Cp}_2\text{Ti}]$  leads to N–H bond activation and formation of the  $\text{Ti}^{\text{IV}}$  intermediate **3** (Scheme 2). Subsequent hydride transfer



**Scheme 2.** Proposed  $\text{Ti}^{\text{IV}}$  (**3**), and isolated  $\text{Zr}^{\text{IV}}$  (**6**, **7**) and  $\text{Ti}^{\text{III}}$  (**8**) amidoborane species.

from boron to the metal was proposed to give the monomeric aminoborane  $\text{Me}_2\text{N}=\text{BH}_2$  (**4**) and the  $\text{Ti}^{\text{IV}}$  species  $[\text{Cp}_2\text{TiH}_2]$ . The former was proposed to dimerize to **2** in an off-metal process, while the latter was expected to release hydrogen to re-form  $[\text{Cp}_2\text{Ti}]$ .<sup>[15]</sup> Chirik and co-workers suggested a similar mechanism, except that B–H bond activation was involved in the first step.<sup>[8]</sup> In contrast, on the basis of detailed kinetic studies, Manners, Lloyd-Jones, and co-workers proposed a two-stage catalytic cycle, with initial formation of the detected linear diborazane  $\text{Me}_2\text{NH}-\text{BH}_2-\text{NMe}_2-\text{BH}_3$  (**5**) after an N–H bond activation step, and subsequent on-metal ring-closing dehydrogenation to give **2**. Once again, the proposed catalytic cycle was postulated to involve the interplay of  $\text{Ti}$  intermediates in the +2 and +4 oxidation states.<sup>[7b]</sup>

Studies on model compounds are expected to provide further insight into the mechanism of these dehydrogenation reactions catalyzed by Group 4 metallocenes. Roesler and co-workers reported a zirconocene(IV) amidoborane complex **6** (Scheme 2), synthesized by reaction of  $[\text{Cp}_2\text{ZrCl}_2]$  with  $\text{H}_3\text{N}\cdot\text{BH}_3$  (2 equiv) in the presence of  $n\text{BuLi}$ .<sup>[12]</sup> Complex **6**, an analogue of **3**, is formally the product of oxidative addition of the N–H bond of ammonia–borane to zirconocene. Very recently, a B-disubstituted analogue of **6**, complex  $[\text{Cp}_2\text{Zr}(\text{H})-$

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$[\text{NH}_2\text{B}(\text{C}_6\text{F}_5)_2\text{H}]$  (**7**), has been reported by Lancaster and co-workers.<sup>[11g]</sup> Interestingly, Wolstenholme, McGrady, and co-workers have isolated a paramagnetic  $\text{Ti}^{\text{III}}$  amidoborane complex (**8**) from the reaction of  $[\text{Cp}_2\text{TiCl}_2]$  with  $\text{Li}[\text{NH}_2\text{BH}_3]$  (2 equiv).<sup>[13]</sup> The latter result suggested that the presence of an  $\text{M}^{\text{III}}$  species under the catalytic dehydrogenation conditions should not be dismissed.

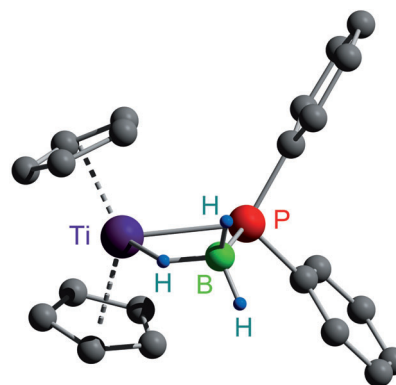
Herein, we report our preliminary studies of the catalytic behavior of a series of Group 4 metallocene complexes with ligands derived from either amine-boranes or the related phosphine-boranes with Ti and Zr in the +3 and +4 oxidation state. Our results suggest that paramagnetic  $\text{M}^{\text{III}}$  species may play a key catalytic role in the dehydrogenation chemistry.

We initially focused on the isolation and characterization of products formed in the stoichiometric version of the catalytic dehydrogenation reaction of **1** (Scheme 1) involving the generation of  $[\text{Cp}_2\text{Ti}]$  in situ. We postulated that the use of a phosphine-borane as substrate might facilitate the isolation of products relevant to prospective reaction intermediates, as phosphine-boranes do not undergo dehydrogenation under these conditions. Indeed, in situ generation of titanocene by the reaction of  $[\text{Cp}_2\text{TiCl}_2]$  with  $n\text{BuLi}$  (2 equiv) in toluene at  $-15^\circ\text{C}$ , followed by addition of  $\text{Ph}_2\text{PH}\cdot\text{BH}_3$  (**9**) at  $22^\circ\text{C}$  led to the isolation of a green solid, which was identified as the titanocene(III) phosphidoborane complex **10** (63% yield; Scheme 3). The same product was obtained by the reaction of  $[\text{Cp}_2\text{TiCl}_2]$  with  $\text{Li}(\text{PPh}_2\text{BH}_3)$  in THF at  $-78^\circ\text{C}$ .

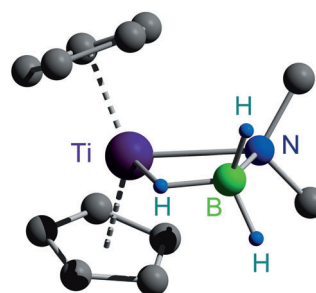
In contrast, attempts to isolate a clean product from the stoichiometric reaction of in situ generated  $[\text{Cp}_2\text{Ti}]$  with  $\text{Me}_2\text{NH}\cdot\text{BH}_3$  were not successful, a result that is not surprising with regard to the efficiency of the analogous catalytic reaction to form **2** (Scheme 1). However, the  $\text{Ti}^{\text{III}}$  complex **11**, an amidoborane analogue of **10**, was obtained from the reaction of  $[\text{Cp}_2\text{TiCl}_2]$  with  $\text{Li}[\text{NMe}_2\text{BH}_3]$  (2 equiv) in THF at  $-78^\circ\text{C}$  (Scheme 3). Complex **11** was isolated as a blue solid in 65% yield, and the aminoborane by-products, primarily **2**, were removed by sublimation.

The molecular structures of complexes **10** and **11** in the solid state were determined by single-crystal X-ray diffraction (Figure 1 and 2). Similar to **6–8**, complexes **10** and **11** feature a planar four-membered Ti-E-B-H ring system involving the metal, the bridging hydrogen atom, the boron atom, and the Group 15 atom (E = P or N).

Because of their paramagnetic nature, complexes **10** and **11** showed no discernible  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR resonances in solution, even at  $-80^\circ\text{C}$ . However, broad  $^{11}\text{B}\{^1\text{H}\}$  NMR



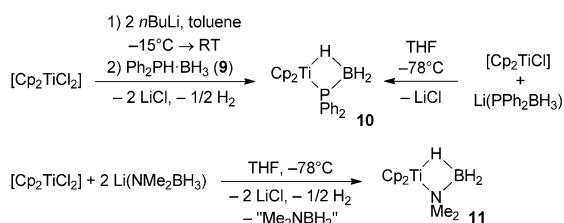
**Figure 1.** Molecular structure of  $\text{Ti}^{\text{III}}$  complex **10** in the solid state (only one of two independent molecules shown; C-bonded hydrogen atoms omitted for clarity).



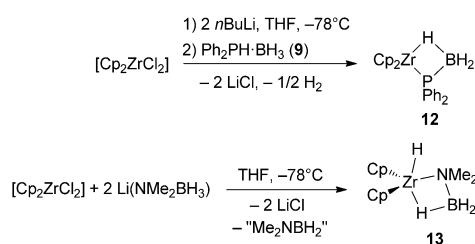
**Figure 2.** Molecular structure of  $\text{Ti}^{\text{III}}$  complex **11** in the solid state (C-bonded hydrogen atoms omitted for clarity).

signals in  $\text{C}_6\text{D}_6$  were detected at  $\delta = -36$  (full width at half maximum (FWHM) = 400 Hz) for **10** and  $\delta = -48$  (FWHM = 2200 Hz) for **11**, respectively (cf. **8**:  $\delta_{\text{B}} = -49$ , broad signal<sup>[13]</sup>). EPR measurements of **10** and **11** in toluene provided  $g_{\text{iso}}$  values of 1.9923 and 1.9899, respectively. The hyperfine splitting pattern showed coupling to a single H nucleus ( $A_{\text{iso}}\{^1\text{H}\} = 4.2 \times 10^{-4} \text{ cm}^{-1}$  in **10**;  $4.6 \times 10^{-4} \text{ cm}^{-1}$  in **11**), thus confirming that the solid-state structure persists in toluene solution. The spectrum of **10** is dominated by the P hyperfine splitting ( $A_{\text{iso}}\{^{31}\text{P}\} = 10.6 \times 10^{-4} \text{ cm}^{-1}$ ), whereas  $^{14}\text{N}$  coupling remains unobserved even at S-band frequency. For comparison, we also recorded the EPR spectrum of complex **8**. This spectrum showed a  $g_{\text{iso}}$  value of 1.9917 and hyperfine coupling to the bridging H ( $4.6 \times 10^{-4} \text{ cm}^{-1}$ ), consistent with structural similarity to complexes **10** and **11** (see Table S1). IR spectra of **8**, **10**, and **11** (in THF) displayed bands characteristic of vibrations of terminal and bridging BH bonds at 2310–2430 and 1810–1820  $\text{cm}^{-1}$ , respectively. The UV/Vis spectra (in THF) showed a single broad low-energy absorption band ( $\lambda_{\text{max}} = 585$  (**8**), 596 (**10**), and 577 nm (**11**); Figure S8, S2, S4), assigned to excitation of the unpaired  $d$  electron. When the samples were exposed to air, a color change from blue (**8** and **11**) or green (**10**) to yellow was observed, and the long-wavelength absorption disappeared (see Figure S9).

In an analogous reaction of  $[\text{Cp}_2\text{ZrCl}_2]$  with  $n\text{BuLi}$  (2 equiv) and **9** at  $-78^\circ\text{C}$  in THF, a brown solid was obtained after work-up and identified as the  $\text{Zr}^{\text{III}}$  phosphidoborane complex **12** (69% yield; Scheme 4). As with **10** and **11**, there



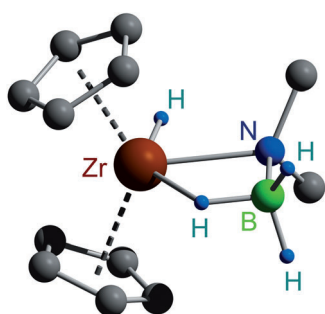
**Scheme 3.** Synthesis of  $\text{Ti}^{\text{III}}$  phosphidoborane complex **10** and  $\text{Ti}^{\text{III}}$  amidoborane complex **11**. By-products have been proposed based on reaction stoichiometry.<sup>[16]</sup>



**Scheme 4.** Synthesis of Zr<sup>III</sup> complex **12** and Zr<sup>IV</sup> complex **13**.

were no discernible <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR signals, but a broad <sup>11</sup>B{<sup>1</sup>H} NMR resonance was detected for **12** ( $\delta = -34$ ; FWHM = 471 Hz). From EPR measurements, a  $g_{\text{iso}}$  value of 1.9884 was obtained and coupling with P and H was observed ( $A_{\text{iso}}\{^{31}\text{P}\} = 25.9 \times 10^{-4} \text{ cm}^{-1}$ ,  $A_{\text{iso}}\{^1\text{H}\} = 15.5 \times 10^{-4} \text{ cm}^{-1}$ ). Further characterization was achieved by IR and UV/Vis spectroscopy, which gave analogous results to **8**, **10**, and **11**.

In contrast to the aforementioned reactions that afforded M<sup>III</sup> complexes **10–12**, the reaction of [Cp<sub>2</sub>ZrCl<sub>2</sub>] with Li[NMe<sub>2</sub>BH<sub>3</sub>] (2 equiv) in THF at  $-78^\circ\text{C}$  afforded the off-white, diamagnetic zirconocene(IV) amidoborane complex **13** in 69% yield of isolated product (Scheme 4). Complex **13** was characterized by multinuclear NMR, IR, and UV/Vis spectroscopy, and a single-crystal X-ray diffraction study (Figure 3). The NMR spectra of **13** showed one set of <sup>1</sup>H, <sup>11</sup>B, and <sup>13</sup>C NMR signals both at ambient temperature and at  $-80^\circ\text{C}$ , irrespective of the solvent employed, consistent with the formation of a single isomer.



**Figure 3.** Molecular structure of Zr<sup>IV</sup> complex **13** in the solid state (C-bonded hydrogen atoms omitted for clarity).

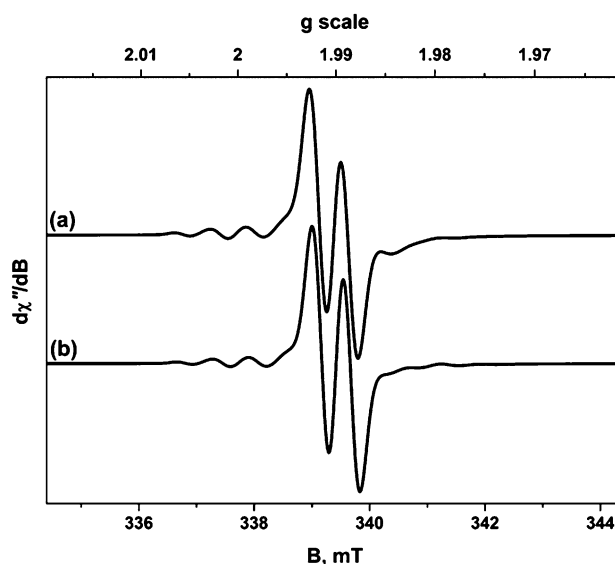
The catalytic activity of the new complexes **10–13** was investigated with respect to the dehydrocoupling/dehydrogenation of **1** in toluene at  $20^\circ\text{C}$  at a 2 mol% precatalyst loading, conditions analogous to those previously used for [Cp<sub>2</sub>Ti]-catalyzed reactions<sup>[7]</sup> (compare with Scheme 1). In each case, reaction monitoring by <sup>11</sup>B NMR spectroscopy indicated the formation of linear diborazane **5** as an intermediate, followed by formation of **2** as the final product. The Ti<sup>III</sup> complexes **10** and especially **11** were found to be highly active precatalysts. Significantly, the activity of **11** toward **1** was comparable to that of in situ generated [Cp<sub>2</sub>Ti] (see Table 1). Furthermore, UV/Vis and EPR spectra were recorded on the reaction solutions derived from **1** and 2 mol% of either complex **11** or [Cp<sub>2</sub>Ti], the latter generated

**Table 1:** Turnover frequencies (TOF) [h<sup>-1</sup>] and conversion after 2 h for catalytic dehydrocoupling of **1** to give **2**.<sup>[a]</sup>

|                           | <b>10</b>         | <b>11</b>         | <b>12</b>         | <b>13</b>        | [Cp <sub>2</sub> Ti] <sup>[b]</sup> |
|---------------------------|-------------------|-------------------|-------------------|------------------|-------------------------------------|
|                           | Ti <sup>III</sup> | Ti <sup>III</sup> | Zr <sup>III</sup> | Zr <sup>IV</sup> |                                     |
| TOF                       | 0.13              | 10.7              | 0.07              | 0.06             | 11.1                                |
| Conversion <sup>[c]</sup> | 83%               | 97%               | 1.5%              | 0                | 88%                                 |

[a] **1** (1.3 M) in toluene,  $20^\circ\text{C}$ , precatalyst (2 mol%, 0.027 M). [b] Generated in situ from [Cp<sub>2</sub>TiCl<sub>2</sub>]/2*n*BuLi. [c] Conversion of **1** after 2 h, measured by <sup>11</sup>B{<sup>1</sup>H} NMR spectroscopy.

in situ from [Cp<sub>2</sub>TiCl<sub>2</sub>] and *n*BuLi (2 equiv). The UV/Vis spectra of both reaction mixtures showed broad peaks at circa 560 nm, which is similar to the spectra of solutions of the isolated Ti<sup>III</sup> complex **11**, within experimental error (see above). Moreover, EPR spectra that were obtained from both reaction solutions (Figure 4) were virtually identical to that of the pure complex **11** (compare with Figure S26). These results are consistent with the presence of the Ti<sup>III</sup> species **11** in both reaction mixtures.



**Figure 4.** X-band EPR spectrum (toluene, 200 K) recorded in situ from the reaction solution of the dehydrocoupling of **1** catalyzed by a) **11** (2 mol%) and b) [Cp<sub>2</sub>Ti] (2 mol%). For experimental conditions, see Figure S32 in the Supporting Information.

The Zr<sup>III</sup> complex **12** also functioned as a precatalyst for the dehydrocoupling of **1**, but was much less active than **10** or **11** (Table 1), and the catalytic efficiency decreased at longer reaction times (Figure S16). By comparison, the Zr<sup>IV</sup> complex **13** showed only very poor activity for the dehydrocoupling of **1**. Thus, while conversions of 83% and 97% for **1** were observed after 2 h with **10** and **11**, respectively, negligible conversion was detected with **13** within the same period (Table 1).

In summary, paramagnetic Ti<sup>III</sup> species, such as **11**, can be isolated from stoichiometric reactions that are analogous to the previously reported catalytic conditions for amine–borane dehydrocoupling using in situ generated [Cp<sub>2</sub>Ti], for which

only  $\text{Ti}^{\text{II}}$  and  $\text{Ti}^{\text{IV}}$  precatalysts and intermediates had been previously invoked. Moreover, the isolated  $\text{Ti}^{\text{III}}$  complexes show activities as precatalysts toward **1** that are similar to those for the latter system.<sup>[17]</sup> Further studies also showed that UV/Vis absorption bands and EPR spectra characteristic of the  $d^1$   $\text{Ti}^{\text{III}}$  species **11** could be detected in the in situ based  $[\text{Cp}_2\text{Ti}]$  reaction mixtures involving **1**. These results indicate that paramagnetic  $\text{Ti}^{\text{III}}$  species may play a key catalytic role in the dehydrogenation chemistry. Our results for isolated model complexes are also consistent with the previous general observations that zirconocene-based precatalysts are less active than those based on Ti. Reasons for this difference will be explored in detail in our future work.

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