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

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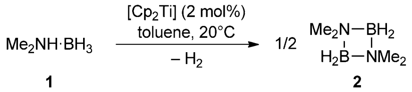
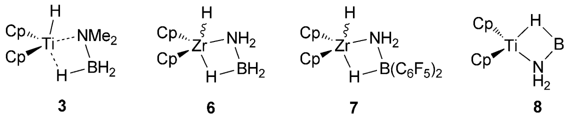
Catalytic dehydrocoupling/dehydrogenation of amine–borane adducts has become a field of rapid growth over the past decade.[1] This development has been driven by potential applications with respect to hydrogen storage,[1,2] transfer hydrogenations and reductions of organic substrates,[3] and the preparation of new inorganic polymeric and solid-state materials.[4,5] A wide variety of catalyst systems have been developed that promote this reaction,[6–10] 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 aminoborane ligands.[11–13] Although much less developed, the catalytic dehydrogenation of phosphine–boranes appears to offer similar potential.[14]

We have previously reported that the first-row Group 4 metallocene [Cp_2Ti], generated in situ from [Cp_2TiCl_2] and *n*BuLi (2 equiv) or, alternatively, from the isolable Ti^{II} precatalyst [$Cp_2Ti(PMe_3)_2$], functions as an efficient homogeneous catalyst for the dehydrogenation of secondary amine–borane adduct **1** to give the cyclodiborazane **2** (Scheme 1).[7] Chirik[8] and, more recently, Rosenthal[9] and co-workers have described analogous studies of a series of active Ti^{II} and Zr^{II} precatalysts for the dehydrocoupling of **1**. In general, the Ti-based precatalysts studied to date were found to be far more active than their Zr-based congeners.



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

Mechanistic proposals for the titanocene-catalyzed dehydrogenation of **1** have differed in many key details, but in all cases, diamagnetic Ti^{II} or Ti^{IV} precatalysts and intermediates have been invoked. For example, based on DFT calculations, Luo and Ohno suggested that interaction of **1** with [Cp_2Ti] leads to N–H bond activation and formation of the Ti^{IV} intermediate **3** (Scheme 2). Subsequent hydride transfer from boron to the metal was proposed to give the monomeric aminoborane $Me_2N{=}BH_2$ (**4**) and the Ti^{IV} species [Cp_2TiH_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 [Cp_2Ti].[15] Chirik and co-workers suggested a similar mechanism, except that B–H bond activation was involved in the first step.[8] 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 $Me_2NH\text{-}BH_2\text{-}NMe_2\text{-}BH_3$ (**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 Ti intermediates in the +2 and +4 oxidation states.[7b]



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

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 [Cp_2ZrCl_2] with $H_3N{\cdot}BH_3$ (2 equiv) in the presence of *n*BuLi.[12] 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 [Cp_2Zr(H)-

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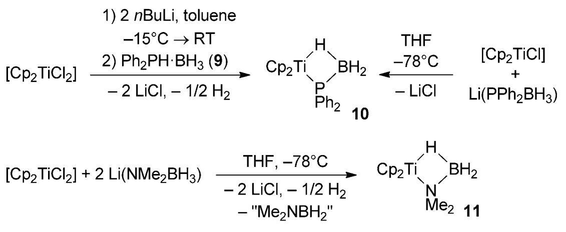
$\{NH_2B(C_6F_5)_2H\}$] (**7**), has been reported by Lancaster and co-workers.[11g] Interestingly, Wolstenholme, McGrady, and co-workers have isolated a paramagnetic Ti^{III} amidoborane complex (**8**) from the reaction of [Cp_2TiCl_2] with Li[NH_2BH_3] (2 equiv).[13] The latter result suggested that the presence of an M^{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 M^{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 [Cp_2Ti] 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 [Cp_2TiCl_2] with *n*BuLi (2 equiv) in toluene at −15 °C, followed by addition of $Ph_2PH{\cdot}BH_3$ (**9**) at 22 °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 [Cp_2TiCl] with Li(PPh_2BH_3) in THF at −78 °C.

In contrast, attempts to isolate a clean product from the stoichiometric reaction of in situ generated [Cp_2Ti] with $Me_2NH{\cdot}BH_3$ 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 Ti^{III} complex **11**, an amidoborane analogue of **10**, was obtained from the reaction of [Cp_2TiCl_2] with Li[NMe_2BH_3] (2 equiv) in THF at −78 °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).



Scheme 3. Synthesis of Ti^{III} phosphidoborane complex **10** and Ti^{III} amidoborane complex. By-products have been proposed based on reaction stoichiometry.[16]

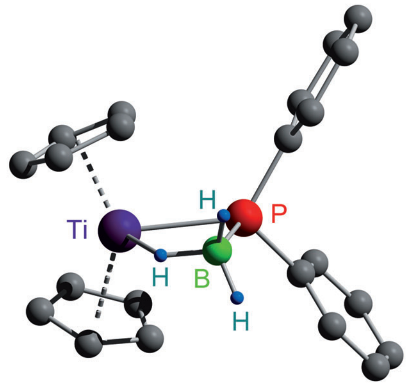


Figure 1. Molecular structure of Ti^{III} complex **10** in the solid state (only one of two independent molecules shown; C-bonded hydrogen atoms omitted for clarity).

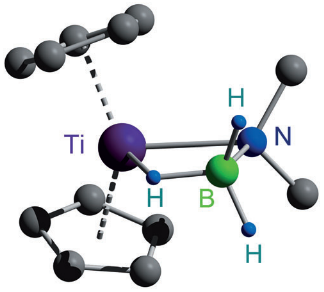
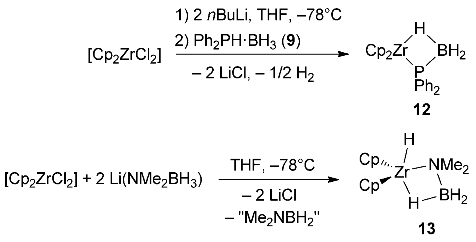


Figure 2. Molecular structure of Ti^{III} complex **11** in the solid state (C-bonded hydrogen atoms omitted for clarity).

Because of their paramagnetic nature, complexes **10** and **11** showed no discernible ^{1}H, ^{13}C, and ^{31}P NMR resonances in solution, even at −80 °C. However, broad $^{11}B\{^{1}H\}$ NMR signals in C_6D_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**: $\delta_B = -49$, broad signal[13]). EPR measurements of **10** and **11** in toluene provided g_{iso} values of 1.9923 and 1.9899, respectively. The hyperfine splitting pattern showed coupling to a single H nucleus ($A_{iso}\{^{1}H\} = 4.2 \times 10^{-4}\ cm^{-1}$ in **10**; $4.6 \times 10^{-4}\ cm^{-1}$ in **11**), thus confirming that the solid-state structure persists in toluene solution. The spectrum of **10** is dominated by the P hyperfine splitting ($A_{iso}\{^{31}P\} = 10.6 \times 10^{-4}\ cm^{-1}$), whereas ^{14}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_{iso} value of 1.9917 and hyperfine coupling to the bridging H ($4.6 \times 10^{-4}\ cm^{-1}$), 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 cm^{-1}, respectively. The UV/Vis spectra (in THF) showed a single broad low-energy absorption band ($\lambda_{max} = 585$ (**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 [Cp_2ZrCl_2] with *n*BuLi (2 equiv) and **9** at −78 °C in THF, a brown solid was obtained after work-up and identified as the Zr^{III} phosphidoborane complex **12** (69 % yield; Scheme 4). As with **10** and **11**, there



Scheme 4. Synthesis of Zr^{III} complex **12** and Zr^{IV} complex **13**.

were no discernible ^{1}H, ^{13}C, and ^{31}P NMR signals, but a broad $^{11}B\{^{1}H\}$ NMR resonance was detected for **12** ($\delta = -34$; FWHM = 471 Hz). From EPR measurements, a g_{iso} value of 1.9884 was obtained and coupling with P and H was observed ($A_{iso}\{^{31}P\} = 25.9 \times 10^{-4}\ cm^{-1}$, $A_{iso}\{^{1}H\} = 15.5 \times 10^{-4}\ cm^{-1}$). 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^{III} complexes **10–12**, the reaction of $[Cp_2ZrCl_2]$ with $Li[NMe_2BH_3]$ (2 equiv) in THF at −78 °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 ^{1}H, ^{11}B, and ^{13}C NMR signals both at ambient temperature and at −80 °C, irrespective of the solvent employed, consistent with the formation of a single isomer.

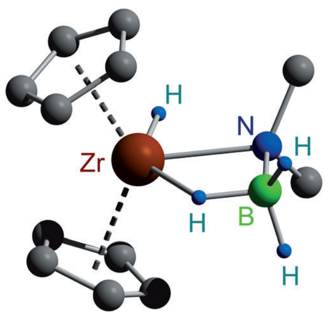


Figure 3. Molecular structure of Zr^{IV} complex **13** in the solid state (C-bonded hydrogen atoms omitted for clarity).

The catalytic activity of the new complexes **10–13** was investigated with respect to the dehydrocoupling/dehydrogenation of **1** in toluene at 20 °C at a 2 mol % precatalyst loading, conditions analogous to those previously used for $[Cp_2Ti]$-catalyzed reactions[7] (compare with Scheme 1). In each case, reaction monitoring by ^{11}B NMR spectroscopy indicated the formation of linear diborazane **5** as an intermediate, followed by formation of **2** as the final product. The Ti^{III} 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 $[Cp_2Ti]$ (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 $[Cp_2Ti]$, the latter generated in situ from $[Cp_2TiCl_2]$ and nBuLi (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^{III} 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^{III} species **11** in both reaction mixtures.

Table 1: Turnover frequencies (TOF) $[h^{-1}]$ and conversion after 2 h for catalytic dehydrocoupling of **1** to give **2**.[a]

	10	**11**	**12**	**13**	$[Cp_2Ti]$[b]
	Ti^{III}	Ti^{III}	Zr^{III}	Zr^{IV}	
TOF	0.13	10.7	0.07	0.06	11.1
Conversion[c]	83 %	97 %	1.5 %	0	88 %

[a] **1** (1.3 M) in toluene, 20 °C, precatalyst (2 mol %, 0.027 M). [b] Generated in situ from $[Cp_2TiCl_2]$/2nBuLi. [c] Conversion of **1** after 2 h, measured by $^{11}B\{^{1}H\}$ NMR spectroscopy.

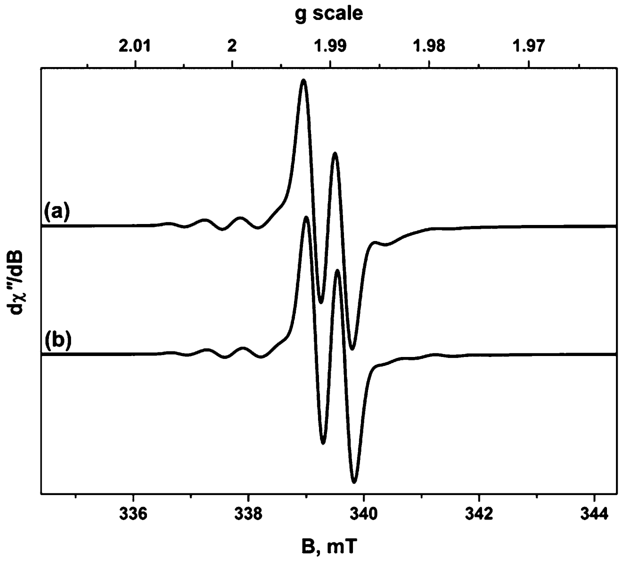


Figure 4. X-band EPR spectrum (toluene, 200 K) recorded in situ from the reaction solution of the dehydrocoupling of **1** catalyzed by a) **11** (2 mol %) and b) $[Cp_2Ti]$ (2 mol %). For experimental conditions, see Figure S32 in the Supporting Information.

The Zr^{III} 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^{IV} 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^{III} 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 $[Cp_2Ti]$, for which only Ti^{II} and Ti^{IV} precatalysts and intermediates had been previously invoked. Moreover, the isolated Ti^{III} complexes show activities as precatalysts toward **1** that are similar to those for the latter system.[17] Further studies also showed that UV/Vis absorption bands and EPR spectra characteristic of the d^1 Ti^{III} species **11** could be detected in the in situ based [Cp$_2$Ti] reaction mixtures involving **1**. These results indicate that paramagnetic Ti^{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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Keywords: amine–boranes · dehydrogenation · metallocenes · phosphine–boranes · transition metals

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[16] The formation mechanisms for **10** and **11** are under further study. Because of the presence of paramagnetic species, the characterization of by-products using NMR spectroscopy is difficult. In addition, the complex nature of the reaction system that involved *n*BuLi and a suspension of [Cp$_2$TiCl$_2$] made it difficult to measure NMR spectra in a J Young NMR tube for detecting H$_2$ evolution. However, significantly, in a reaction of [Cp$_2$Ti(PMe$_3$)$_2$] and Ph$_2$PH·BH$_3$ in [D$_8$]toluene, which results in formation of complex **10**, evolution of H$_2$ could be detected in the ^{1}H NMR spectrum. See the Supporting Information for further details.

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