

Homogeneous, Titanocene-Catalyzed Dehydrocoupling of Amine–Borane Adducts

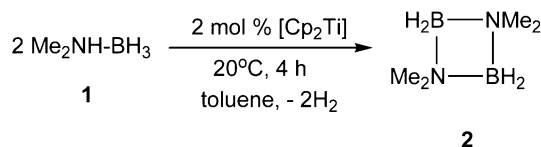
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Transition-metal-catalyzed reactions revolutionized the field of organic chemistry in the latter half of the 20th century. In comparison, the use of transition metals to promote reactions which generate new bonds between main group elements is an underdeveloped field with considerable potential.¹ We have previously reported the dehydrocoupling of phosphine– and amine–borane adducts by late transition metal (e.g., Rh) catalysts.^{2–4} This new chemistry is of significance from the perspective of current interest in hydrogen storage,⁵ hydrogen transfer reactions,⁶ and the formation of new inorganic polymers.^{7,8} We have also described our detailed studies of the mechanism of these reactions and provided evidence that in the case of the dehydrocoupling of phosphine–borane adducts the mechanism is a homogeneous process while that for amine–borane adducts appears to be predominantly heterogeneous.^{3b} In this preliminary report, we describe the discovery that *early* transition metal metallocene complexes can act as highly active, *homogeneous* dehydrocoupling catalysts toward amine–borane adducts.⁹

We previously showed that Ti(IV) catalysts, such as Cp₂TiMe₂, are inactive toward the dehydrocoupling of both phosphine– and amine–borane adducts.^{2b,3a} For example, treatment of Me₂NH–BH₃ (**1**) with a catalytic amount of Cp₂TiMe₂ at 25 °C for 160 h resulted in no reaction by ¹¹B NMR spectroscopy.^{3a} Interestingly, Corey and co-workers have developed the dehydrocoupling of secondary silanes using [Cp₂M] (M = group 4 metal) catalysts which are generated *in situ* by the reaction of the appropriate Cp₂MCl₂ complex with 2 equiv of ⁿBuLi.¹⁰ To investigate if catalysts of this type would be active for other systems, such as group 13/15 adducts, we treated **1** with a catalytic (2 mol %) amount of [Cp₂Ti]. In performing this reaction, extensive bubbling and H₂ release was observed, and full conversion to **2** was detected by ¹¹B NMR spectroscopy in only 4 h (Scheme 1).¹¹

Scheme 1



The exact details of the reaction between Cp₂TiCl₂ and ⁿBuLi are not known with certainty, but presumably Cp₂TiⁿBu₂ is generated slowly followed by the formation of the putative Ti(II) product “Cp₂Ti”.¹² Presumably the electron-deficient, coordinatively unsaturated Ti center in the latter facilitates an initial reaction with **1** and entry into the catalytic cycle. Of potential relevance to this chemistry is the report by Sneddon and co-workers that hydroboration reactions of decaborane with terminal olefins can be promoted by a Ti(II) catalyst, Cp₂Ti(CO)₂.¹³

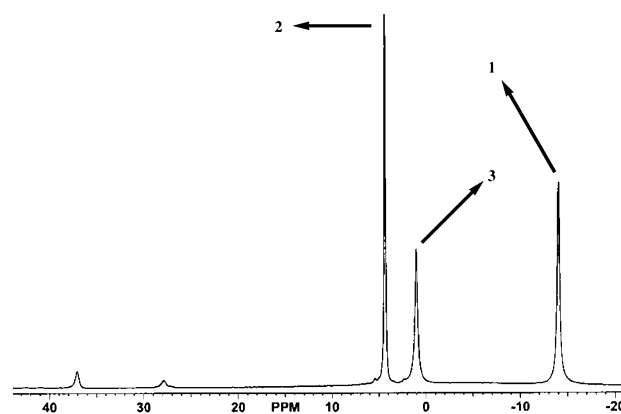
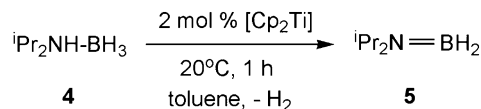
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Figure 1. ¹¹B NMR spectrum (toluene, 96 MHz) of a mixture containing **1** and [Cp₂Ti] (2 mol %) after 40 min reaction time with various species assigned. The small resonance at 28 ppm corresponds to (Me₂N)₂BH.¹⁵

Interestingly, another signal is generated in the ¹¹B NMR spectrum at 1 ppm during the course of the reaction of **1** with catalytic amounts of [Cp₂Ti] and is presumably an intermediate or byproduct (Figure 1). Moreover, this resonance splits into a triplet when the ¹H-coupled spectrum is recorded (¹J_{B–H} = 108 Hz). On the basis of the proximity of the chemical shift to that of the cyclic borazane [MeNH–BH₂]₃ (¹¹B δ: –5 ppm) and the observation of an identical coupling constant, we tentatively propose that this species is the cyclic borazane [Me₂N–BH₂]₃ (**3**). Further evidence for this conclusion is given by the fact that the difference in chemical shift between **1** and **3** is equal to that between MeNH₂·BH₃ and [MeHN–BH₂]₃ (14 ppm). Cyclic trimer **3** may be initially generated before complete disproportionation occurs, affording **2** as the more thermodynamically stable product. Significantly, a small resonance was also noted at 37 ppm, and this can be assigned to monomeric Me₂N=BH₂, a possible precursor to both **2** and **3**.¹⁴

We proceeded to investigate whether [Cp₂Ti] would also act as a dehydrocoupling catalyst for more sterically encumbered amine–boranes, such as ⁱPr₂NH–BH₃ (**4**). We have previously shown that **4** dehydrocouples in the presence of colloidal Rh(0) to slowly yield the monomeric species ⁱPr₂N=BH₂ (**5**)¹⁶ over 4 days at 20 °C.^{3a} Significantly, treatment of **4** with 2 mol % of [Cp₂Ti] resulted in full conversion to **5** in only 1 h (Scheme 2), verifying the high catalytic activity of this early transition metal system.

Scheme 2



The mechanism for this Ti-catalyzed process is of considerable interest. A key initial question is whether the reaction is heterogeneous or homogeneous.¹⁷ The previously described dehydrocou-

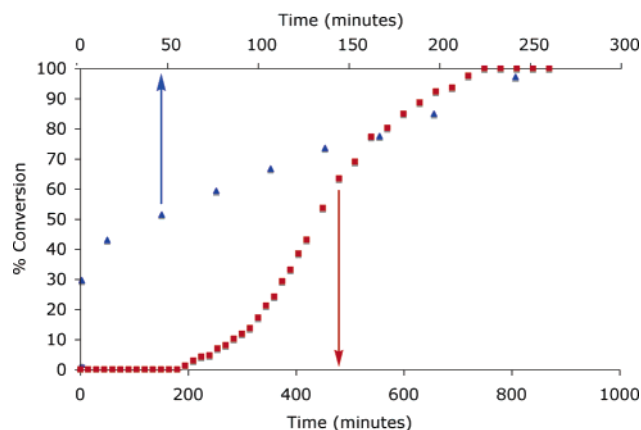


Figure 2. Graph of % conversion versus time for the catalytic dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ using $[\{\text{Rh}(\text{1,5-cod})(\mu\text{-Cl})_2\}]^{3b}$ (ca. 2 mol % of Rh, toluene, 20 °C, red curve, squares) and $[\text{Cp}_2\text{Ti}]$ (ca. 2 mol % of Ti, toluene, 20 °C, blue curve, triangles).

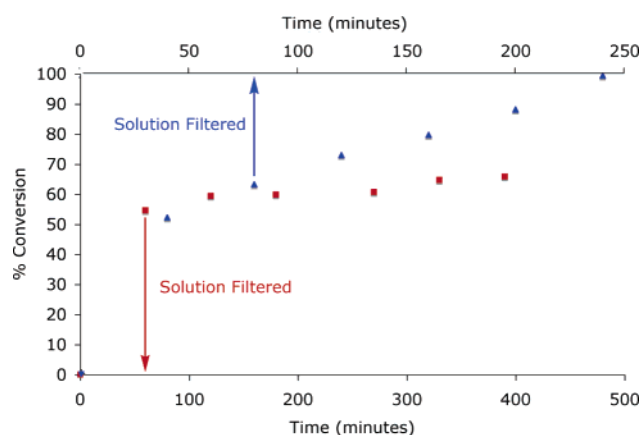


Figure 3. Graph of % conversion versus time for the catalytic dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ using $\text{Rh}/\text{Al}_2\text{O}_3^{3b}$ (ca. 2 mol % of Rh, toluene, 20 °C, red curve, squares) and $[\text{Cp}_2\text{Ti}]$ (ca. 2 mol % of Ti, toluene, 20 °C, blue curve, triangles). The solutions were filtered at the times indicated.

pling of **1** using Rh(I) precatalysts showed a sigmoidal-shaped kinetic profile characteristic of a heterogeneous process with an induction period prior to Rh colloid generation.³ In contrast, for the dehydrocoupling with $[\text{Cp}_2\text{Ti}]$, there is an initial rapid consumption of **1** over 15 min followed by an approximately linear conversion versus time plot (Figure 2).

Further insight was provided by poisoning experiments with mercury, a well-known poison of heterogeneous metal catalysts, owing to its adsorption onto the catalyst surface or formation of an amalgam.¹⁸ In contrast to the Rh-catalyzed dehydrocoupling of **1**, which is completely halted by the addition of Hg,³ the Ti-catalyzed reaction is unaffected even by a large excess of the metal. A further indication that the latter is a homogeneous process was provided by filtration experiments. These involved filtering the reaction mixture through a small pore membrane in order to distinguish between soluble and insoluble catalysts.¹⁷ If the activity is dramatically lowered upon filtration, then an insoluble heterogeneous catalyst is assumed. Significantly, for the Ti-catalyzed reaction, filtration of the catalytically active solution through a 0.2 μm filter after 80 min reaction time resulted in no detectable suppression in activity, and the reaction still proceeded to completion after 240 min.¹⁹ In contrast, for the Rh-catalyzed case, the reaction rate is dramatically suppressed (Figure 3).

Recently, we showed that the Rh-catalyzed dehydrocoupling of **1** can function as a transfer hydrogenation to deliver a stoichiometric

amount of H_2 to olefins.⁶ To explore whether the Ti-catalyzed system behaves similarly, **1** was treated with a catalytic amount of $[\text{Cp}_2\text{Ti}]$ in the presence of cyclohexene. After 16 h, the ^{11}B and ^1H NMR spectra indicated that dehydrocoupling to yield **2** and hydrogenation to cyclohexane had proceeded quantitatively. This underscores the potential of this new early transition metal system as a viable, highly active alternative to its Rh counterpart.

Further studies will target a full exploration of the generality and utility of the Ti-catalyzed dehydrocoupling reaction and detailed understanding of the mechanism which shows the signatures of a homogeneous process.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) For reviews on metal-catalyzed dehydrocoupling, see: (a) Gauvin, F.; Harrod, J. F.; Woo, H. G. *Adv. Organomet. Chem.* **1998**, *42*, 363. (b) Reichl, J. A.; Berry, D. H. *Adv. Organomet. Chem.* **1998**, *43*, 197. (c) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22. (d) Jaska, C. A.; Bartolotti-Scott, A.; Manners, I. *Dalton Trans.* **2003**, 4015.
- (2) For reports on the late transition-metal-catalyzed dehydrocoupling of phosphine–borane adducts, see: (a) Dorn, H.; Singh, R. A.; Massey, J. A.; Lough, A. J.; Manners, I. *Angew. Chem., Int. Ed.* **1999**, *38*, 3321. (b) Dorn, H.; Singh, R. A.; Massey, J. A.; Nelson, J. M.; Jaska, C. A.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 6669. (c) Clark, T. J.; Rodezno, J. M.; Clendenning, S. B.; Aouba, S.; Brodersen, P. M.; Lough, A. J.; Ruda, H. E.; Manners, I. *Chem.—Eur. J.* **2005**, *11*, 4526.
- (3) For reports on the late transition-metal-catalyzed dehydrocoupling of amine–borane adducts, see: (a) Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2003**, *125*, 9424. (b) Jaska, C. A.; Manners, I. *J. Am. Chem. Soc.* **2004**, *126*, 9776.
- (4) For another recent report on late transition-metal-catalyzed dehydrocoupling of amine–borane adducts, see: Chen, Y.; Fulton, J. L.; Linehan, J. C.; Autrey, T. *J. Am. Chem. Soc.* **2005**, *127*, 3254.
- (5) (a) Jacoby, M. *Chem. Eng. News* **2005**, *83*, 42. (b) Gutowski, M.; Autrey, T. *Chem. World* **2005**, *3*, 44. (c) Bluhm, M. E.; Bradley, M. G.; Butterick, R., III; Kusari, U.; Sneddon, L. G. *J. Am. Chem. Soc.* **2006**, *128*, 7748.
- (6) Jaska, C. A.; Manners, I. *J. Am. Chem. Soc.* **2004**, *126*, 2698.
- (7) Dorn, H.; Rodezno, J. M.; Brunnhöfer, B.; Rivard, E.; Massey, J. A.; Manners, I. *Macromolecules* **2003**, *36*, 291.
- (8) Jacquemin, D.; Lambert, C.; Perpète, E. A. *Macromolecules* **2004**, *37*, 1009.
- (9) Baker et al. recently briefly described a homogeneous Cu catalyst for the dehydrocoupling of $\text{Me}_2\text{NH}\cdot\text{BH}_3$: (a) Baker, R. T. Plenary Lecture, *Inorganic Discussion Weekend*, London, Ontario, Canada Nov. 2005. (b) Baker, R. T. Personal communication to I.M.
- (10) (a) Corey, J. Y.; Zhu, X. H.; Bedard, T. C.; Lange, L. D. *Organometallics* **1991**, *10*, 924. (b) Corey, J. Y.; Huhmann, J. L.; Zhu, X. H. *Organometallics* **1993**, *12*, 1121.
- (11) As a control, no reaction was observed when **1** was treated with a catalytic amount of $n\text{BuLi}$.
- (12) Hitchcock, P. B.; Kerton, F. M.; Lawless, G. A. *J. Am. Chem. Soc.* **1998**, *120*, 10264.
- (13) Pender, M. J.; Carroll, P. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **2001**, *123*, 12222.
- (14) Nöth, H.; Vahrenkamp, H. *Chem. Ber.* **1967**, *100*, 3353.
- (15) Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer-Verlag: Berlin, 1978.
- (16) Compound **5** has found use in the Pd-catalyzed borylation of aryl halides. See: Euzenat, L.; Horhant, D.; Ribourdouille, Y.; Duriez, C.; Alcaraz, G.; Vaultier, M. *Chem. Commun.* **2003**, 2280.
- (17) Widegren, J. A.; Finke, R. G. *J. Mol. Catal. A: Chem.* **2003**, *198*, 317.
- (18) (a) Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855. (b) Whitesides, G. M.; Hackett, M.; Brainard, R. L.; Lavallée, J.-P. P. M.; Sowinski, A. F.; Izumi, A. N.; Moore, S. S.; Brown, D. W.; Staudt, E. M. *Organometallics* **1985**, *4*, 1819.
- (19) Colloidal Ti(0) nanoparticles are also inactive as catalysts. See Supporting Information for experimental details.

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