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--amine--borane adducts by late transition metal (e.g., Rh) catalysts.2,3 For example, treatment of Me2NH-BH3 with 2 mol % of [Cp2Ti] resulted in no reaction by 11 B NMR spectroscopy.3a Interestingly, another signal is generated in the 11 B 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(â,â) = 108 Hz). On the basis of the proximity of the chemical shift to that of the cyclic borazane [Me2NH-BH2]3 (11 B 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 (4) and [MeN-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 Pr2NH=BH2 (4). We have previously shown that 4 dehydrocouples in the presence of colloidal Rh(0) to slowly yield the monomeric species Pr2N=BH2 (5)16 over 4 days at 20 °C.3a

The exact details of the reaction between Cp2TiCl2 and BuLi are not known with certainty, but presumably Cp2Ti2Bu2 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

Scheme 1

\[ 2 \text{Me}_2\text{NH-BH}_3 \xrightarrow{2 \text{ mol } \% \text{[Cp}_2\text{Ti]} \atop 20^\circ \text{C}, 4 \text{ h} \text{ toluene, -H}_2} \text{H}_2\text{B}\text{NMe}_2 \]

\[ \text{Me}_2\text{N-BH}_2 \]

Scheme 2

\[ \text{Pr}_2\text{NH-BH}_3 \xrightarrow{2 \text{ mol } \% \text{[Cp}_2\text{Ti]} \atop 20^\circ \text{C}, 1 \text{ h} \text{ toluene, -H}_2} \text{Pr}_2\text{N=BH}_2 \]

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amount of H₂ to olefins. To explore whether the Ti-catalyzed system behaves similarly, I was treated with a catalytic amount of [Cp₂Ti] in the presence of cyclohexene. After 16 h, the ¹¹B 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


11. As a control, no reaction was observed when I was treated with a catalytic amount of BuLi.


19. Colloidal Ti(0) nanoparticles are also inactive as catalysts. See Supporting Information for experimental details.

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