On Hydroborations of Alkenes Catalyzed by Titanium Complexes

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Abstract: Literature reports of hydroborations of alkenes by borohydride anion "catalyzed" by titanium complexes are investigated to test for the formation of borane as an intermediate.

Three papers by Isagawa and co-workers reported additions of borohydride anion to alkenes are catalyzed by titanium complexes.¹⁻³ In a typical experiment,¹ 5 mol % of Cp₂TiCl₂ was added to LiBH₄ (1 equivalent) in THF, and stirred for 1 h at room temperature giving a violet solution and dihydrogen; 1-octene was then added, and the mixture was maintained at 45 °C for 21 h. 1-Octanol was the major product after oxidation with basic hydrogen peroxide. It was suggested that this process involves catalyzed addition of borohydride to alkenes giving alkylborohydride intermediates (reaction 1).



These titanium mediated hydroborations appear to offer an alternative to hydroborations catalyzed by rhodium (+1) complexes. However, the reaction of Cp₂TiCl₂ with borohydride is known to produce borane,^{4,5} as outlined below (reaction 2),⁵ and borane therefore should be produced in reaction 1.



In fact, 0.05 equivalents of catalyst could produce 0.025 equivalents of diborane, which in turn could account for hydroboration of 0.15 equivalents of the alkene substrate. In other reports, 2,3 20 mol % of catalyst was

used which would provide enough borane to hydroborate 60 % of substrate. These concerns, especially in the light of the results presented in the previous paper, led us to investigate whether the hydroboration step is really titanium catalyzed, or if the Cp_2TiCl_2 simply mediates formation of borane which then serves as the exclusive hydroborating agent.

The titanium borohydride Cp₂Ti(μ -H)₂BH₂ is strongly implicated in reaction 1. For the current study, it was prepared and isolated via the *Inorganic Synthesis* procedure.⁵ This violet complex is extremely airsensitive; it rapidly turns yellow in the presence of trace oxygen, even in the solid state.

Results obtained using Cp₂Ti(μ -H)₂BH₂ to mediate hydroboration reactions are shown in the Table, along with data from other sources. Entries 1 and 2 show Cp₂Ti(μ -H)₂BH₂ promotes hydroboration of phenylethene with and without added lithium borohydride. Surprisingly, the reaction mediated by a catalytic amount of Cp₂Ti(μ -H)₂BH₂ is appreciably *faster* than the corresponding transformation mediated by 1 equivalent of the complex without lithium borohydride (entry 2). Entries 1 - 4 reveal Cp₂Ti(μ -H)₂BH₂ and lithium borohydride give a different ratio of regioisomeric alcohols when compared with borane with and without lithium borohydride, whereas stoichiometric Cp₂Ti(μ -H)₂BH₂ with phenylethene affords the same ratio. The ratio of regioisomers obtained using catalytic Cp₂Ti(μ -H)₂BH₂ with lithium borohydride (entry 1) is almost the same as that observed previously² when Cp₂TiCl₂ was used as a catalyst (entry 5). Significantly, other work by Isagawa *et al* (entries 6 and 7) proved that the titanium mediated reactions give different facial selectivities in the hydroboration of β -pinene when compared with the reaction in which BH₃ was used as the reagent (formed *in situ* from borohydride and boron trifluoride etherate).³

Isagawa and co-workers proposed that the products of the titanium mediated reactions are alkylborohydrides on the basis of the observation that no migration products were observed at 150 °C, whereas internal alkylboranes migrate to terminal isomers under these conditions.⁶ To test this hypothesis, we studied mixtures of phenylethene, Cp₂Ti(μ -H)₂BH₂, and lithium borohydride (ratio 100:5:110) by ¹¹B NMR. A significant quantity of lithium borohydride (δ = -41 ppm, quintet) remained after all the alkene had reacted, and two sharp resonances at δ = -12 and -14 ppm were observed. These chemical shifts are typical for trialkylborohydrides, but extensive decoupling experiments (to be described in a full paper on this work) indicate *the products of the titanium mediated hydroboration reaction are predominantly tetraalkylborates*, *not trialkylborohydrides*.⁷⁻⁹ Throughout, no trace of BH₃ or trialkylboranes were detected in the catalyzed processes, and only traces of trialkylborohydrides.

Even the small amounts of trialkylborohydrides observed in the catalyzed process are not derived from uncatalyzed hydroboration of the substrate by *in situ* BH₃, as shown by the following experiments. First, a THF solution of lithium borohydride and Cp₂Ti(μ -H)₂BH₂ (ratio 2:1) heated to 65 °C for 12 h did not give borane in concentrations that were conveniently detected by ¹¹B NMR. Secondly, when two mixtures of triethylborane and lithium borohydride (ratio 1:1) in THF were maintained for 4 h at 65 °C, one in the presence of Cp₂Ti(μ -H)₂BH₂ (5 mol %), no triethylborohydride was observed (¹¹B NMR) in either case.

In conclusion, hydroborations of phenylethene by lithium borohydride mediated by 5 mol % Cp₂Ti(μ -H)₂BH₂, do not involve BH₃ to any appreciable extent. The products are predominantly tetraalkylborates



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Table. Hydroboration Reactions Promoted by Titanium Complexes.

^a Product ratios accessed by GC and by NMR after work-up A, silylation and calibration, . ^b 94 % conversion after 9 h at 65 °C. ^c 80 % conversion after 19 h at 65 °C. ^d At 25 °C. ^e Work-up B. ^f The reactive species is BH₃.¹⁰

(BR4⁻), and little or no borane or alkylboranes are produced. Moreover, alkylboranes were not converted to alkylborohydrides under the reaction conditions.

The relatively slow reaction of Cp₂TiBH₄ with phenylethene in the absence of borohydride implies that this complex is not involved in the iterative steps of the catalytic processes, or that borohydride is involved in the rate determining step of the catalytic cycle. That hydroboration of phenylethene by Cp₂TiBH₄ in the absence of borohydride gives the same ratio of regioisomers as BH₃ implies the reaction could occur via slow thermal degradation of the complex into borane and titanium hydrides.¹¹ Unfortunately, this assertion is difficult to test by ¹¹B NMR since Cp₂Ti(μ -H)₂BH₂ is paramagnetic.

If Cp₂Ti(μ -H)₂BH₂ is a precursor to a catalytically active complex, what is this complex? It is known that lithium borohydride and Cp₂Ti(μ -H)₂BH₂ combine in a dynamic process which forms a bis(borohydride) complex in a equilibrium that favors the starting materials (reaction 3).⁴

 $Cp_2Ti(\mu-H)_2BH_2$ + $LiBH_4$ - Li $[Cp_2Ti(BH_4)_2]$ (3)

As a working hypothesis, we speculate that this bis(borohydride) complex could be critical in these titanium catalyzed hydroborations. The mechanism of formation of tetraalkylborates in these processes remains to be elucidated.

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