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Titanium-Mediated Additions of Borohydride to Alkenes

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Abstract: This paper concerns additions of borohydride to alkenes promoted by titanium complexes. Isolated $Cp_2Ti(\mu\text{-}H)_2BH_2$ was shown to be a catalyst precursor for the hydroboration of phenylethene by borohydride. Lithium borohydride appears to be involved in the formation of the true catalytically active complex since borohydride/catalytic $Cp_2Ti(\mu\text{-}H)_2BH_2$ mixtures gave faster hydroboration than stoichiometric $Cp_2Ti(\mu\text{-}H)_2BH_2$ in the absence of borohydride. Furthermore, the catalytic and stoichiometric titanium-mediated hydroboration of phenylethene provided different regioselectivities. Regio- and/or stereoselectivities for the hydroboration of phenylethene and β-pinene also differ when mediated by BH_4^-/catalytic $Cp_2Ti(\mu\text{-}H)_2BH_2$, or by BH_3 generated *in situ*. Extensive ^{11}B NMR experiments indicate the predominant products in the hydroboration of phenylethene with borohydride are tetraalkylborates; minor amounts of alkylborohydrides are formed (mostly trialkylborohydride) and little or no alkylboranes. Alcohols are formed in the transformations mediated by BH_4^-/catalytic $Cp_2Ti(\mu\text{-}H)_2BH_2$, after treatment with basic peroxide, but these result from oxidation of alkylborohydride intermediates since tetraalkylborates oxidize very slowly under the conditions used. A mechanism is proposed for the hydroboration of phenylethene mediated by $Cp_2Ti(\mu\text{-}H)_2BH_2$; this involves abstraction of BH_3 from the complex by borohydride leading to a titanium hydride species, conventional hydroboration of the alkene by BH_3, insertion of phenylethene into the titanium–hydride bond, and then alkyl-transfer from titanium to boron giving tetraalkylborates. Differences for the hydroboration of other substrates are discussed also. 1-Decene and β-pinene react slower than phenylethene in reactions promoted by BH_4^-/catalytic $Cp_2Ti(\mu\text{-}H)_2BH_2$, and monoalkylborohydrides or boranes tend to be the predominant products. These alkenes gave little or no tetraalkylborates, possibly due to the relatively slow insertion of these alkenes into titanium–hydride bonds or because of lack of titanium-to-boron alkyl transfer.

Background

Transition metal-catalyzed hydroborations are useful alternatives to classical (uncatalyzed) additions of boranes to alkenes and alkynes.[1] Most of the catalyzed hydroborations reported to date involve complexes of late transition metals in a low oxidation state,[2–14] but there are some notable exceptions. First, catecholborane additions can be accelerated by lanthanide cyclopentadienyl complexes, in which the key step is believed to be combination of a lanthanide alkyl complex with the boron-hydride via a four-center transition state.[15] Furthermore, lanthanide salts have also been reported to promote the hydroboration of alkenes with catecholborane.[16] Second, a series of reactions, reported by Isagawa and co-workers, involve additions of *borohydride* to alkenes mediated by bis(cyclopentadienyl)dichlorotitanium (Cp_2TiCl_2) (Scheme 1).[17–19]

Nearly[8] all rhodium-catalyzed hydroboration reactions are complicated by disproportion of catecholborane and complex organometallic transformations,[20,21] so they are hard to define and harder to manipulate into highly stereoselective transformations.[13] Titanium-mediated hydroborations, however, are potentially useful since the mechanism of these reactions must be different to the rhodium-catalyzed processes. Certainly, use of borohydride circumvents the complications associated with disproportionation of catecholborane, and since BH_4^- is a fundamental building block from which both diborane and catecholborane are made, the economic advantages and convenience of using borohydride are significant.

Despite their potential, an enigma surrounds the titanium-mediated hydroboration reactions: the mechanistic pathway(s) by which borohydride adds to alkenes. Isagawa *et al.* speculated that these reactions occur via addition of free borohydride to a titanium alkene complex.[19] They also concluded the products are alkylborohydrides (*i.e.* $LiR_nBH_{(4-n)}$ from $LiBH_4$) on the basis of the following experiment: 2-octene reacted with lithium borohydride at 45 °C and at 150 °C in the presence of Cp_2TiCl_2 giving significant amounts of 2-octanol after oxidation. 2-Octylborane is known to isomerize to 1-octylborane at 150 °C,[22] so it could not have been an organoborane that was oxidized. Furthermore, the titanium-mediated hydroboration of alkynes followed by protonolysis of the intermediates gave alkene products. This is different to the reaction of these substrates with BH_3,

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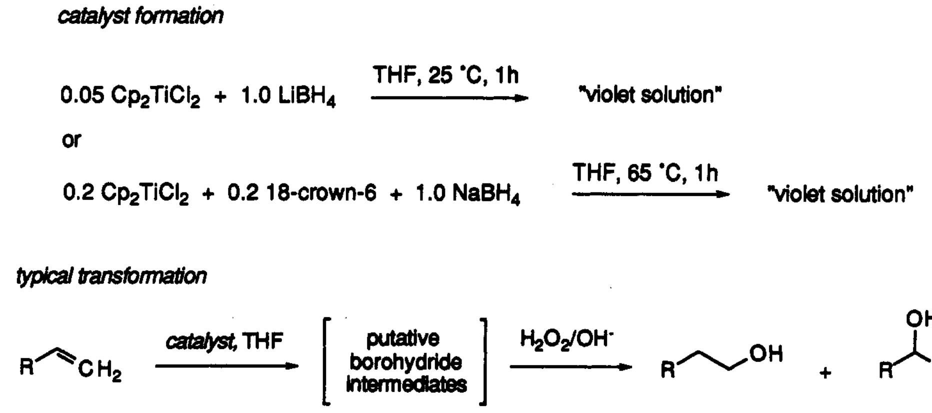
Scheme 1. Original Reports of Titanium-Mediated Hydroborations



which usually produces dihydroboration products, suggesting that BH_3 is not the reactive species in the catalyzed process.

Two types of reaction conditions were used in Isagawa's original work on Cp_2TiCl_2-promoted hydroborations (Scheme 1). In one typical experiment,[17] 5 mol % of Cp_2TiCl_2 was added to a solution of *ca.* 1 equiv (based on substrate) of $LiBH_4$ in THF and stirred under argon for 1 h. A violet solution was formed. The alkene substrate was then added and the reaction mixture was stirred at 45–65 °C for 21 h or more. In the second modification,[18] 20 mol % Cp_2TiCl_2, 20 mol % 18-crown-6, and 1 equiv of $NaBH_4$ were stirred at 65 °C for 1 h. A violet solution again formed. The substrate was added, and the reaction mixture was stirred at 65 °C for 5 or 24 h. None of the reaction intermediates were characterized.

Stoichiometric reactions of Cp_2TiCl_2 with borohydride have been studied in detail by other groups (reaction 1).[23,24] This transformation was reported to produce diborane as a byproduct. The protocols summarized above make no mention of steps to remove the diborane that must have been produced in the catalyst formation steps. Consequently, despite Isagawa's assertions that borohydrides are formed, the conditions of the reaction suggest that some of the substrate should be consumed by diborane to give alkylboranes in transformations that do not intimately involve the metal. Specifically, 15 mol % uncatalyzed hydroboration could occur if 5 mol % of catalyst was used and 60 mol % if 20 mol % of catalyst was used.

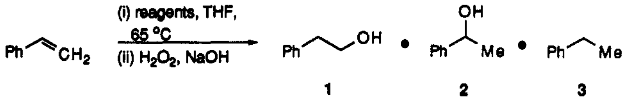
$$2Cp_2TiCl_2 + 4NaBH_4 \underset{\text{ca. 4 h}}{\overset{\text{DME, 25 °C}}{\rightarrow}} 2Cp_2Ti(\mu\text{-}H)_2BH_2 + B_2H_6 + 4NaCl + H_2 \quad (1)$$

In summary, the mechanism of Cp_2TiCl_2-promoted hydroborations was unclear, and there were reasons to suspect they even might not involve catalysis of the B–H addition step. Therefore, titanium-mediated hydroborations merited further investigations.[25] This paper describes fundamental mechanistic probes and attempts to dispel some of the ambiguities associated with these reactions.

Results and Discussion

Reactions of $Cp_2Ti(\mu\text{-}H)_2BH_2$ and Phenylethene under Catalytic and Stoichiometric Conditions. Reaction 1 indicates $Cp_2Ti(\mu\text{-}H)_2BH_2$ is produced under conditions used in the "catalyst formation" step of the original titanium-mediated hydroborations. Isagawa and co-workers observed the catalyst solution was violet, which is the color of this titanium complex. Consequently, $Cp_2Ti(\mu\text{-}H)_2BH_2$ is strongly implicated for reactions in which Cp_2TiCl_2 is the starting material for the catalyst formation.

Table 1. Regioselective Hydroboration of Phenylethene Promoted by Titanium Complexes



entry	reagents, equiv	1:2	1:2:3	% yield	% conversion	time (h)
1	0.05 Cp_2TiBH_4 1.0 $LiBH_4$	69:31	58:26:16	51	94	9
2	1.0 Cp_2TiBH_4	83:17	66:14:20	60	80	19
3[b]	1.0 BH_3	81:19	81:19:0	90	100	2
4	0.2 BH_3 1.0 $LiBH_4$	82:18	82:18:trace	85	100	2
5[18]	0.2 Cp_2TiCl_2 1.0 $NaBH_4$ 0.2 18-crown-6	69:31	69:31:*d*	70	*d*	5

[a] Product ratios accessed by ^1H NMR and by GC after silylation and calibration. [b] At 25 °C. [c] At 30 °C. [d] No data reported by Isagawa and co-workers.

As a starting point in the current work, $Cp_2Ti(\mu\text{-}H)_2BH_2$ was synthesized via an *Inorganic Syntheses* procedure.[23] The formation reaction can be performed using Schlenk line techniques, but the complex must be isolated in a glove box due to its sensitivity to air. Traces of oxygen rapidly transform the violet complex into a yellow material.

Pure, isolated, $Cp_2Ti(\mu\text{-}H)_2BH_2$ indeed promoted additions of lithium borohydride to alkenes; for instance, GC experiments indicate 5 mol % of this material mediated 94% consumption of phenylethene after 9 h at 65 °C. Almost identical product distributions were obtained using catalytic $Cp_2Ti(\mu\text{-}H)_2BH_2$ with lithium borohydride (Table 1, entry 1) compared with the original work wherein Cp_2TiCl_2 was used (entry 5).[18,19] The transformation was slower, however, when a full equivalent of $Cp_2Ti(\mu\text{-}H)_2BH_2$ *and no borohydride* was used (only 80% conversion after 19 h at 65 °C, entry 2). The significant difference between these two sets of conditions is also apparent from the product distributions: more primary alcohol is formed (after oxidation) when 1.0 equiv of catalyst and no borohydride is used. Comparison of entries 1 and 3 reveal hydroboration of phenylethene using $Cp_2Ti(\mu\text{-}H)_2BH_2/LiBH_4$, and using BH_3·THF, gave different ratios of regioisomeric alcohols. Stoichiometric $Cp_2Ti(\mu\text{-}H)_2BH_2$ hydroborated phenylethene with the same regioselectivity as BH_3·THF, however. Incidentally, borohydride and borane combine to form equilibrium amounts of $B_2H_7^-$,[26] but this makes no difference to the regioselectivity of the hydroboration of phenylethene with BH_3·THF because both BH_3 and BH_3/BH_4^- give the same ratio of regioisomers (entries 3 and 4).

Identification of the Organoboron Products before Oxidation. Isagawa originally proposed lithium alkylborohydrides, not

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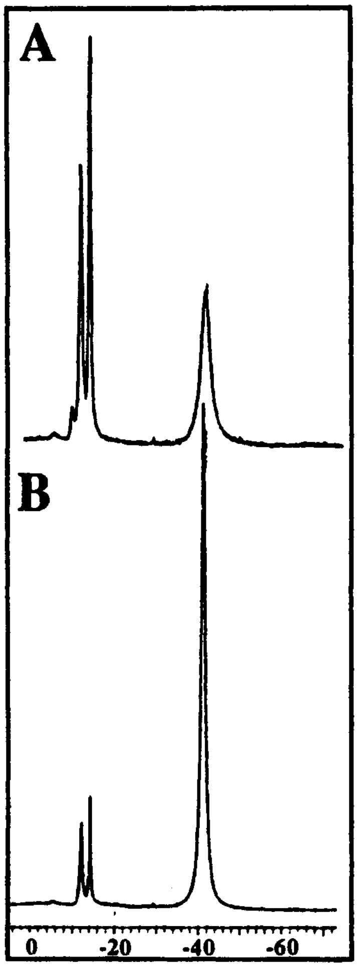

Figure 1. A: $\{^1H\}^{11}B$ NMR of 5 equiv of phenylethylene, 1 equiv of $LiBH_4$, and 0.05 equiv of Cp_2TiBH_4 after 12 h at 65 °C. B: $\{^1H\}^{11}B$ NMR of 1 equiv of phenylethene, 1 equiv of $LiBH_4$, and 0.05 equiv of Cp_2TiBH_4 after 12 h at 65 °C.

alkylboranes, were formed in the reactions they studied since one organoboron product did not isomerize at 150 °C. However, the method used to form the catalysts implied the products could be alkylboranes from uncatalyzed BH_3 additions (*vide supra*). Identification of the organoborane products therefore was crucial to further comprehend these reactions.

In the current work, the catalytic reaction was monitored by ^{11}B NMR. A mixture of phenylethene, 1.0 equiv of $LiBH_4$, and 0.05 equiv of $Cp_2Ti(\mu\text{-}H)_2BH_2$ after 9.5 h in THF showed a considerable amount of residual $LiBH_4$ and peaks at δ −14.4 and −12.3 ppm, characteristic of alkylborohydrides or tetraalkylborates. When more phenylethene was added, the $LiBH_4$ peak diminished, the resonances at −14.4 and −12.3 ppm were enhanced, and minor peaks at −10.1 ppm and −5.4 (doublet) emerged. No splitting was observed for the predominant peaks in the corresponding coupled spectrum (Figure 1 shows the coupled spectra).

Alkylborohydrides were formed via a different synthetic route to determine if these were the products of this catalyzed hydroboration as originally proposed. Thus phenylethene was reacted with borane in THF, and excess alkene was used to ensure conversion to trialkylboranes. If the ratio of anti-Markovnikoff-to-Markovnikoff hydroboration is approximately 4:1 (*cf*. Table 1, entry 3), then the ratio of the trialkylboranes formed would be very roughly 64:16:4:1 for $B(CH_2CH_2Ph)_3$:$B(CH_2CH_2Ph)_2(CH(Me)Ph)$:$B(CH_2CH_2Ph)(CH(Me)Ph)_2$:$B(CH(Me)Ph)_3$. The ^{11}B NMR of this mixture was totally uninformative since the peaks were extremely broad and ill-defined. However, the reaction was then "quenched" by adding $LiAlH_4$/DABCO to convert the alkylboranes to the corresponding trialkylborohydrides (reaction 2).[27,28] The spectrum of the mixture formed after this process is shown in Figure 2B. There are three conspicuous peaks in this spectrum (δ −13.5 {broad}, −9.7 {sharp}, −5.7 {minor}) presumably corresponding to $LiHB(CH_2CH_2Ph)_3$, $LiHB(CH_2CH_2Ph)_2(CH(Me)Ph)$, and $LiHB(CH_2CH_2Ph)(CH(Me)Ph)_2$. All these peaks are doublets ($J_{B\text{-}H}$ = 78 ± 3 Hz) in the coupled spectrum. As far as we are aware, this is the first application of $LiAlH_4$/DABCO quenching to ^{11}B NMR spectroscopy, although this technique and other approaches have been used as preparative methods for the production of alkylborohydrides.[27-30] It is extremely effective and proved invaluable throughout this work.

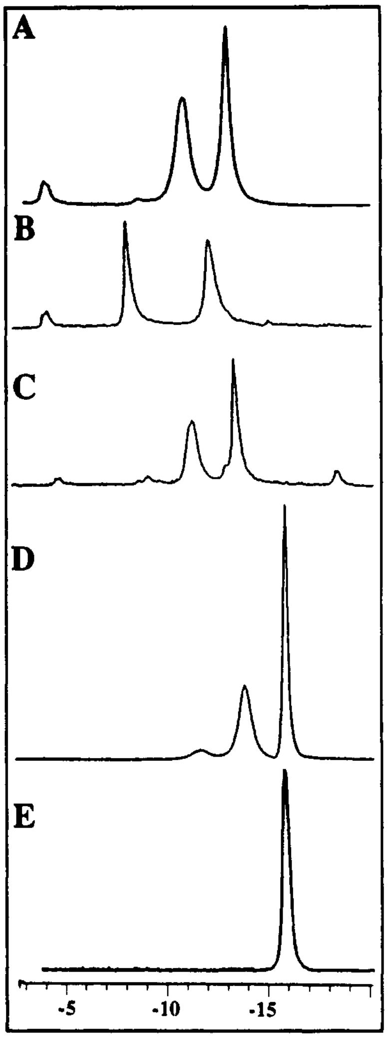

Figure 2. Proton-boron decoupled ^{11}B NMR spectra from the following: A. Hydroboration of 2 equiv of phenylethene by 1 equiv of $LiBH_4$ catalyzed by 0.05 equiv of Cp_2TiBH_4 after 12 h at 65 °C. B. Hydroboration of 3.3 equiv of phenylethene by 1 equiv of BH_3·THF complex followed by treatment with $LiAlH_4$/DABCO. C. Reaction mixture from spectrum A treated with $LiAlH_4$/DABCO. D. Hydroboration of 3.3 equiv of phenylethene by 1 equiv of BH_3·THF complex followed by treatment of 1 equiv of (2-phenylethyl)lithium. E. Lithium tetra(2-phenylethyl)boronate from (2-phenylethyl)lithium and BF_3·Et_2O.

Alkylborohydrides were not the major products formed in the titanium-mediated reactions, because the spectra shown in Figures 2A (from the catalyzed reaction) and 2B (from R_3BH^--mixtures) are not even similar. Chemical shifts for the major peaks are different, and in the former case no splitting is evident in the proton–boron coupled spectrum. The absence of splitting could

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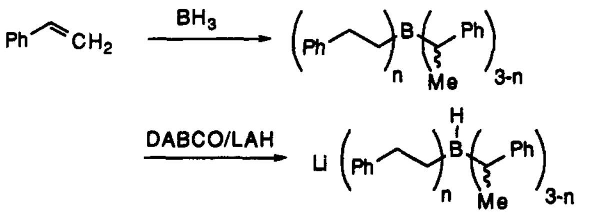
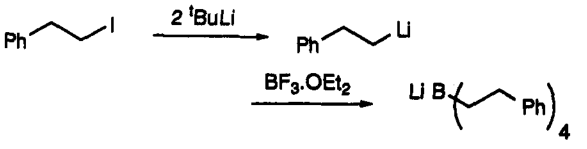


(2)

be due to rapid exchange processes (*e.g.* between trialkylboranes and "ate-complexes"), which have been reported to broaden peaks in ^{11}B NMR, alter chemical shifts, and suppress coupling.[31,32] Such equilibria are unlikely in the sample corresponding to Figure 2B since all the products were converted to alkylborohydrides via the addition of $LiAlH_4$/DABCO.[27,28,33] It was possible, however, that exchange processes could have had a bearing on the spectrum shown in Figure 2A, so the sample from the catalyzed hydroboration was also treated with $LiAlH_4$/DABCO to quench exchange phenomena (Figure 2C). It gave almost the same ^{11}B NMR as shown in Figure 2A; the predominant peaks in the original spectrum were unchanged and were still singlets in the proton-coupled spectrum. Minor shoulders at −9.7 and −13.6 ppm (both doublets) and a small triplet at −18.8 ppm were observed also. Therefore, differences between the spectra in Figure 2, parts A and B, are not due to exchange phenomena.

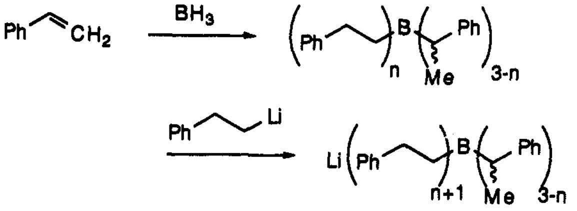
The results up to this point indicate *the predominant products of the titanium-mediated catalyzed hydroboration of phenylethene were not alkylboranes (from uncatalyzed addition of BH_3), and they were not the alkylborohydrides originally postulated.*

If not alkylboranes or alkylborohydrides, what were the major products formed in titanium-promoted hydroboration of phenylethene? Tetraalkylborates were prepared to test for the presence of these by comparison. Thus, 2-lithiophenylethane was made from 2-phenylbromoethane[34] and from 2-phenyliodoethane[35,36] in two sets of experiments. Both these samples of $PhCH_2CH_2Li$ were transformed into $LiB(CH_2CH_2Ph)_4$ via reaction with $BF_3{\cdot}OEt_2$ (reaction 3).



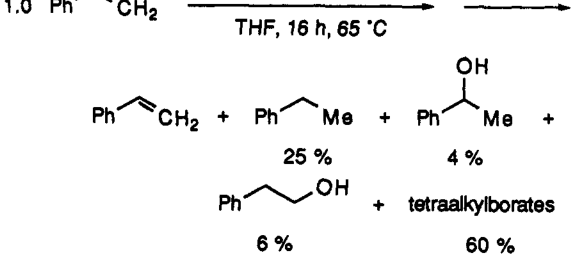
(3)

Analysis of samples from both these transformations by ^{11}B NMR showed sharp resonances at δ −16.3 ppm (Figure 2D),[37] which does not quite correspond to the major peak in Figure 2A. However, the "all-terminal" borate is not necessarily a major product in this process, since the titanium-mediated hydroboration of phenylethene gives a *ca* 7:3 mixture of primary/secondary alcohols after oxidation. Therefore, a mixture of isomers of $LiB(CH_2CH_2Ph)_4$ was prepared by treatment of borane with excess phenylethene to give a mixture of isomeric trialkylboranes {probably including $B(CH_2CH_2Ph)_3$, $B(CH_2CH_2Ph)_2(CH(Me)Ph)$, $B(CH_2CH_2Ph)(CH(Me)Ph)_2$, and $B(CH(Me)Ph)_3$}; this mixture was then reacted with $PhCH_2CH_2Li$ to give the corresponding tetraalkylborates (reaction 4). The ^{11}B NMR spectrum of this mixture in Figure 2E matches well with Figure 2A except that $LiB(CH_2CH_2Ph)_4$ (−16.3 ppm) was not formed in the catalytic reaction, and the relative concentrations of the other peaks are different. We conclude, *the most conspicuous products in the ^{11}B NMR spectrum of the titanium promoted hydroboration of phenylethene were regioisomeric tetraalkylborates.*



(4)

Tetraalkylborates are not easily oxidized to alcohols.[38] For example, when the crude reaction mixture represented in Figure 2A was treated with 30% H_2O_2/3 M NaOH (25 °C, 12 h) the ^{11}B NMR showed only changes corresponding to transformation of BH_4^- and trialkylborohydrides (−5.4 ppm) into $B(OH)_3$; the resonances assigned to tetraalkylborates (−14.4, −12.3, and −10.1) did not decrease appreciably relative to a $BF_3{\cdot}OEt_2$ standard. Formation of tetraalkylborates therefore should lead to decreased yields of product alcohols. To accentuate the production of tetraalkylborates, phenylethene was reacted with only 0.5 equiv of $LiBH_4$ instead of 1.0 equiv which had been used for the reactions discussed so far. When the crude reaction mixture was oxidized, *ca.* 60% of the phenylethene could not be accounted for in GC analyses. The implication of these observations is that 60% of the phenylethene is converted into tetraalkylborates as indicated in reaction 5, resulting in lower yield of alcohols and producing relatively more hydrogenation product.



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The quenching experiments with $LiAlH_4$/DABCO as described above exposed organoboron compounds which were previously "^{11}B NMR invisible" due to exchange processes. However, it was still necessary to check for alkylborohydrides with ^{11}B NMR chemical shifts close to the putative tetraalkylborates, since overlap potentially could have obscured alkylborohydride signals in the quenching experiments. Therefore, the reaction mixture resulting from catalyzed hydroboration of borohydride with phenylethene was reacted with ethanol to transform all alkylborohydrides into ethyl boronates and ethyl borinates which resonate in a different region of a ^{11}B NMR spectrum. New ^{11}B NMR peaks were seen corresponding to $B(OEt)_3$ (19.5 ppm), $RB(OEt)_2$ (32.5 ppm), and $R_2B(OEt)$ (52.5 ppm). The latter compounds could be derived from reaction of ethanol with $LiBH_3R$ and $LiBH_2R_2$, respectively, or these mono- and dialkylboronate esters could have been produced from RBH_2 and R_2BH. Experiments to differentiate between these possibilities are described in the next section. However, it is significant that the observations described so far indicate that dialkylborohydrides were observed in Figure 2C (minor triplet at −18.8 ppm) after $LiAlH_4$/DABCO quench of the crude metal promoted reaction, but monoalkylborohydrides were not.

Exchange Processes Involving Alkylboranes and Alkylborohydrides. Alcohols formed in the titanium-mediated hydroboration processes could have been derived from either alkylboranes

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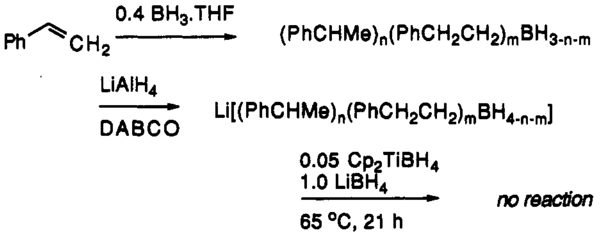
(38) Damico, R. *J. Org. Chem.* **1964**, *29*, 1971.

or alkylborohydrides, but not from tetraalkylborates (*vide supra*). Indeed, the experiments outlined in the previous sections indicate that one or both these compound types were present. Throughout, rapid chemical exchange on the NMR time scale could have precluded observation of some critical peaks, so limiting the value of direct ^{11}B NMR experiments. In fact, proton–boron-coupled ^{11}B NMR spectra of the crude reaction mixtures from the catalyzed hydroboration of phenylethene showed broad non-coupled BH_4^- resonances and no coupling was observed, whereas this signal normally appears as a well-defined quintet in the coupled spectrum. In view of this evidence that exchange *is* occurring, it was extremely important to establish what exchange processes may have been operative in the metal-promoted reactions to deduce what signals might have been lost. This section describes experiments undertaken to investigate possible exchange pathways.

First, the following experiment proves that *exchange processes between alkylboranes and borohydride are very likely.* When phenylethene was treated with a deficiency of BH_3 (0.35 equiv), the ^{11}B NMR spectrum indicated the products were predominantly trialkylboranes (broad singlet at 84 ppm in the proton-boron-coupled ^{11}B NMR) and dialkylboranes (broad singlet at 54 ppm). Then catalytic $Cp_2Ti(\mu\text{-}H)_2BH_2$/stoichiometric BH_4^- was added and the mixture was maintained at 65 °C for 12 h. The ^{11}B NMR of this material at ambient temperature was completely different to that before addition of the titanium complex. Predominant peaks in the reaction after the addition were a number of weak, ill-defined broad singlets at 55, 32, 9, and –18.6 ppm in addition to a broad singlet corresponding to $LiBH_4$. Consequently, exchange processes between BH_4^- and alkylboranes had been established. In the preliminary communication of this work, we described experiments which illustrated triethylborane was not involved in rapid exchange with borohydride in the presence of $Cp_2Ti(\mu\text{-}H)_2BH_2$.[25] These observations are not contradictory because dialkylboranes, rather than exclusively trialkylboranes, were involved in the current experiments, and this may be a significant difference.[39]

In contrast to BH_4^-/alkylborane exchange phenomena, the following experiment indicates *alkylborohydrides and lithium borohydride in the presence of $Cp_2Ti(\mu\text{-}H)_2BH_2$ do not interconvert rapidly on the NMR time scale.* Thus a mixture of lithium dialkyl- and trialkylborohydrides was prepared from phenylethene in the two-step sequence shown in reaction 6. These gave three doublets in the ^{11}B NMR (–5.8, –9.9, and –13.6 ppm) and two triplets (–14.0 and -19.1 ppm). Then $LiBH_4$ and $Cp_2Ti(\mu\text{-}H)_2BH_2$ were added and the mixture was stirred at 65 °C for 21 h. After this period the ^{11}B NMR at 25 °C was virtually unchanged: all the signals were still observable and splittings were well resolved in the boron–proton-coupled spectrum. This indicates that alkylborohydrides do not rapidly equilibrate with lithium borohydride under the titanium-mediated reaction conditions. Furthermore, no changes were observed in the ratios of the original signals within experimental limits, therefore isomerization of the alkylborohydrides had not occurred.

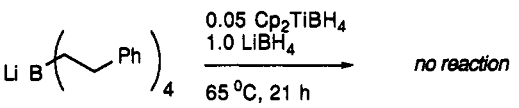


(6)

In summary, the experiments described in this section reveal that alkylboranes in the titanium-mediated reactions would be obscured by exchange phenomena. Conversely, alkylborohydrides should be conspicuous in ^{11}B NMR spectra of the titanium-mediated hydroboration of phenylethene unless alkylboranes are present (*cf.* others have demonstrated alkylboranes/alkylborohydride exchange can occur).[31,32]

Isomerization Experiments with Tetraalkylborates from Phenylethene. Various experiments were performed to test for possible isomerization processes that could influence the regioselectivity of the titanium-mediated hydroboration of phenylethene. The first experiment was to check for concomitant isomerization in the exchange of alkylboranes with $LiBH_4$. Phenylethene was treated with a deficiency of BH_3 (0.35 equiv), catalytic $Cp_2Ti(\mu\text{-}H)_2BH_2$, and 1.0 equiv of lithium borohydride, and the mixture was maintained at 65 °C for 12 h. The ratio of 2-phenylethanol to 1-phenylethanol after oxidation was 80:20 (GC). Hydroboration of phenylethene with BH_3 is known to give this ratio of regiosiomers (Table 1, entry 3), hence the product distribution was unaffected by treatment with the titanium catalyst and borohydride in the present experiment. Equilibration of alkylborane intermediates therefore cannot be invoked to account for the different ratios for the primary and secondary product alcohols for titanium-catalyzed and BH_3 hydroboration of phenylethene (*cf.* Table 1, entries 1 and 3).

The previous sections showed that alkylboranes and alkylborohydrides obtained from phenylethene do not isomerize under the titanium-mediated hydroboration conditions, but is this also true for tetraalkylborates? For instance, it was possible that $LiB(CH_2CH_2Ph)_4$ was not observed in the crude reaction mixture due to isomerization to regioisomeric borates, $LiB(CH_2CH_2Ph)_n(CH(Me)Ph)_{4-n}$. To test this, $LiB(CH_2CH_2Ph)_4$, prepared via reaction 3, was subjected to the titanium-mediated hydroboration conditions (reaction 7). The only boron-containing species observed (^{11}B NMR) were $LiB(CH_2CH_2Ph)_4$ and $LiBH_4$. Thus *isomerization processes do not influence the regioselectivity of the $Cp_2Ti(\mu\text{-}H)_2BH_2$-promoted hydroboration of phenylethene.*



(7)

Time Dependence of Tetraalkylborate Production. Figure 3A–C shows concentration changes of phenylethene, tetraalkylborates, and ethylbenzene during the hydroboration of phenylethene with $LiBH_4$ in the presence of catalytic $Cp_2Ti(\mu\text{-}H)_2BH_2$. Two notable qualitative features are apparent from these data. First, no appreciable induction time was observed. Second, tetraalkylborates are formed even at the very earliest stages of the reaction, implying that trialkylborohydrides, or other lesser substituted borates, do not accumulate.

The Catalyst System: ^{11}B NMR and Homogeneity Investigations. It was possible that the role of lithium borohydride in the catalytic reaction was to reduce $Cp_2Ti(\mu\text{-}H)_2BH_2$ to colloidal titanium metal, especially since a similar reaction has been reported for $TiCl_4$ and $LiEt_3BH$.[40,41] Heterogeneous catalysis by titanium metal was therefore a possibility. In the stoichiometric reaction, gradual decomposition of $Cp_2Ti(\mu\text{-}H)_2BH_2$ to $BH_3\cdot THF$ (and titanium hydrides) could account for the relatively sluggish consumption of phenylethene. ^{11}B NMR and homogeneity studies were performed specifically to address these issues and to obtain more information in general.

The complex $Cp_2Ti(\mu\text{-}H)_2BH_2$ is paramagnetic; hence it is inconspicuous in NMR experiments, at least in THF and other ethereal solvents.[24] Thus, only a broad borohydride resonance was detected in the ^{11}B NMR spectrum of a mixture of 1.0 equiv

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[39] We did not establish if the catalysts is actively involved in these exchange processes.

[40] Bönnemann, H.; Brijoux, W.; Joussen, T. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 273.

[41] Bönnemann, H.; Korall, B. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1490.

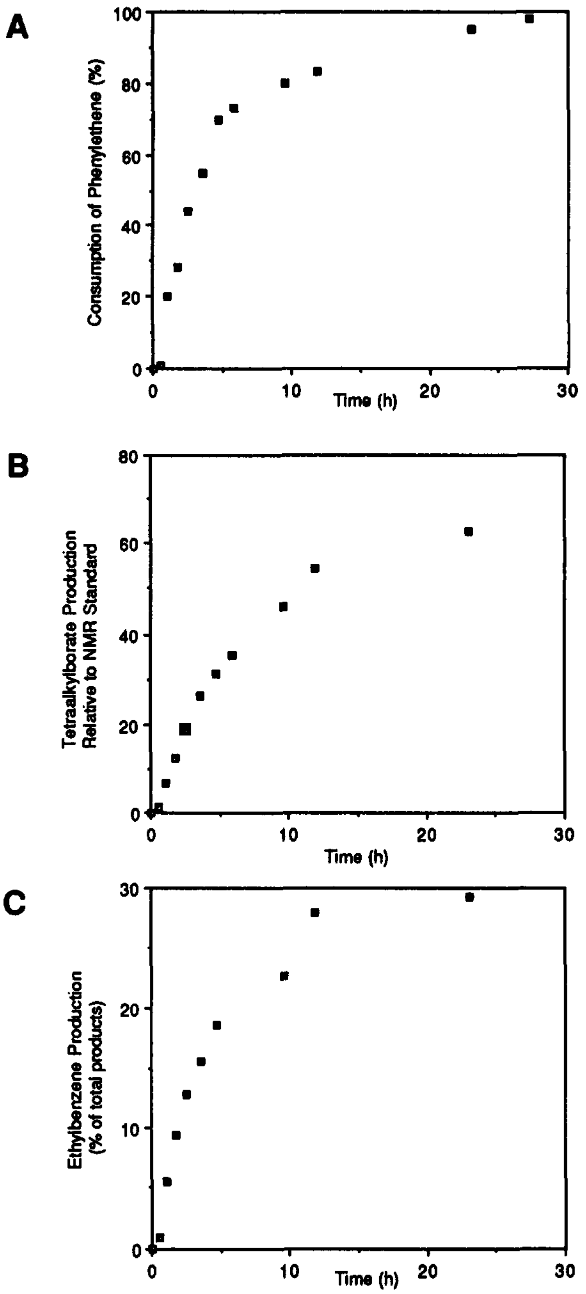
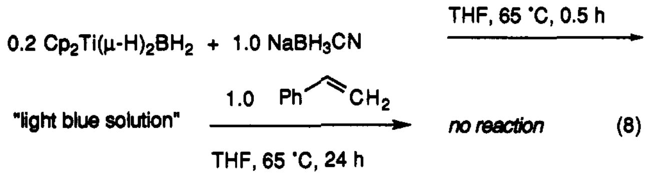


Figure 3. Time dependence of $Cp_2Ti(\mu\text{-}H)_2BH_2$ (0.05 equiv)-catalyzed hydroboration of phenylethene (2 equiv) with $LiBH_4$ (1 equiv). A: Consumption of phenylethene *vis* time. B: Production of combined regioisomeric tetraalkylborates *vis* time. C: Production of ethylbenzene *vs* time.

of $Cp_2Ti(\mu\text{-}H)_2BH_2$ and 2.0 equiv of $LiBH_4$ after 12 h at 65 °C. If $BH_3{\cdot}THF$ was formed in this mixture, it was present in amounts smaller than the ^{11}B NMR detection limits. Similarly, when $Cp_2Ti(\mu\text{-}H)_2BH_2$ was heated alone (no $LiBH_4$) for 12 h at 65 °C, no signals at all were detected.

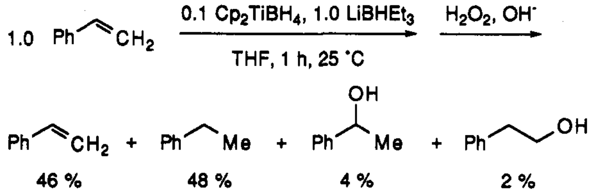
In general, as the $Cp_2Ti(\mu\text{-}H)_2BH_2$ mediated hydroborations proceeded, the solution changed from bright violet to deep blue purple, and some solid material was deposited on the sides of the flask. To test homogeneity, two identical hydroborations of phenylethene were performed in parallel, except mercury was added to just one. The reaction rates and product distributions were followed by GC. Both transformations proceeded at approximately the same rate, and the product distribution was identical (*i.e.* that shown in Table 1, entry 1). These observations imply that the catalysis is homogeneous assuming that titanium metal does amalgamate under these conditions, *i.e.* that the "classical" mercury test[42] is valid in this particular reaction.[43]

Use of Other Borohydrides with $Cp_2Ti(\mu\text{-}H)_2BH_2$ and Phenylethene. It was of interest to investigate other borohydrides for possible hydroborations of alkenes mediated by $Cp_2Ti(\mu\text{-}H)_2BH_2$. Consequently, a reaction using sodium cyanoborohydride was briefly investigated. A light blue solution formed immediately when 0.05 equiv of $Cp_2Ti(\mu\text{-}H)_2BH_2$ was mixed with 1.0 equiv of $NaBH_3CN$ at 65 °C. There was no reaction when 1.0 equiv of phenylethene was added to this solution (GC *vs* internal standard).



(8)

Possibly the lack of reactivity described above was due to some fundamental structural difference between complexes of BH_4^- and BH_3CN^-. With regard to this, it may be significant that Lippard has concluded cyanoborohydride tends to coordinate to transition metals via the nitrogen atom.[44] Consequently, a reaction was attempted using $LiBHEt_3$ as the borohydride source, since this has no *N*-coordinating group. Addition of this compound (1.0 equiv) to 0.1 equiv of $Cp_2Ti(\mu\text{-}H)_2BH_2$ gave a brown solution. A rapid reaction ensued at 25 °C when 1.0 equiv of the phenylethene substrate was added to this solution. Most of the phenylethene consumed was converted to phenylethane, the *hydrogenation* product as indicated in reaction 9. The reactions with $LiHBEt_3$ were not pursued further since the amounts of hydroboration products in these processes are relatively low.



(9)

Proposed Mechanism for Titanium-Mediated Hydroboration of Phenylethene. A rationale to explain the observed characteristics of the $Cp_2Ti(\mu\text{-}H)_2BH_2$-catalyzed hydroboration of phenylethene with $LiBH_4$ needs to accommodate the following experimental observations: (i) the reaction of phenylethene with $Cp_2Ti(\mu\text{-}H)_2BH_2$ proceeds faster under catalytic conditions (*i.e.* in the presence of excess borohydride) than under stoichiometric conditions (*i.e.*without borohydride); (ii) regiochemistries for titanium-mediated and BH_3 hydroboration of phenylethene are different, giving relatively more secondary alcohol for the catalyzed reaction; (iii) the observed products of $Cp_2Ti(\mu\text{-}H)_2BH_2$-mediated hydroboration of phenylethene are lithium trialkylborohydrides and lithium tetraalkylborates, which are produced from the very start of the transformation; (iv) alkylborohydrides or tetraalkylborates derived from phenylethene do not isomerize under the reaction conditions; and, (v) Isagawa's hydroboration of phenylethene mediated by Cp_2TiCl_2 gave higher yield and a faster reaction rate than the corresponding $Cp_2Ti(\mu\text{-}H)_2BH_2$-promoted reaction in the current work.

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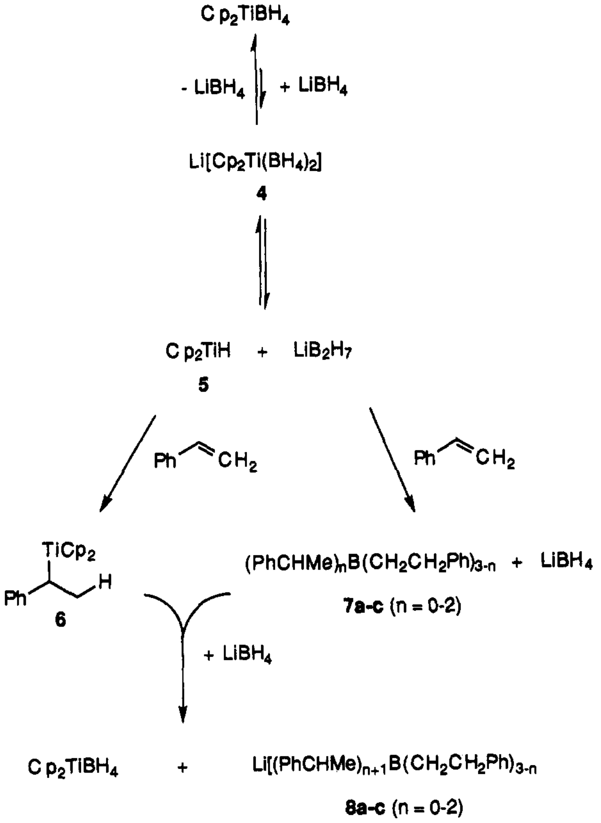
(42) Whitesides, G. M.; Hackett, M.; Brainard, R. L.; Lavayelle, J.-P. P. M.; Sowinski, A. F.; Izumi, A. N.; Moore, S. S.; Brown, D. W.; Staudt, E. M. *Organometallics* **1985**, *4*, 1819.

(43) EPR experiments showed identical signals before and after completion of the reaction. This result also is indicative that reduction of the titanium-(III)-complex to titanium metal does not take place under the reaction conditions.

(44) Lippard, S. J.; Welcker, P. S. *Chem. Commun.* **1970**, 515.

Scheme 2. Proposed mechanism for the formation of tetraalkylborates in the $Cp_2Ti(\mu\text{-}H)_2BH_2$-mediated hydroboration of phenylethene.



A mechanism that meets all of the criteria listed above is shown in Scheme 2. Lithium borohydride and $Cp_2Ti(\mu\text{-}H)_2BH_2$ combine in a dynamic process that forms the bis(borohydride) complex **4** in an equilibrium favoring the starting materials.[24] We speculate that this complex could dissociate into the titanium hydride **5** and LiB_2H_7. Such BH_3-abstraction from metal–borohydride complexes by Lewis bases has been observed previously for zirconium–borohydride complexes.[45] Thermal decomposition of metal-borohydride complexes into BH_3 and metal hydrides is also well established and could be an alternative pathway.[46] The LiB_2H_7 formed reacts rapidly with phenylethene to produce several isomeric boranes **7** and $LiBH_4$. Meanwhile, highly regioselective insertion of phenylethene into the titanium hydride bond of **5** produces the titanium–alkyl complex **6**. Borohydride then displaces the alkyl group which is simultaneously transferred to the boron atom of boranes **7**. This produces isomeric borates **8** with regeneration of the catalyst. Titanium hydride **5** could be responsible for the observed competitive hydrogenation (*cf.* Table 1).[47–49]

Excess $LiBH_4$ is needed for the abstraction of BH_3 from $Cp_2Ti(\mu\text{-}H)_2BH_2$, so reactions in the absence of $LiBH_4$ would be expected to proceed through a different reaction pathway. Indeed, the slower reaction rate observed in the stoichiometric reactions of $Cp_2Ti(\mu\text{-}H)_2BH_2$ and phenylethene in the absence of excess $LiBH_4$ (Table 1, entry 2) is consistent with the fact that the first step in Scheme 2 is not possible under noncatalytic reaction conditions.

The proposed high regioselectivity of alkene insertion into the titanium hydride bond of **5** in favor of the secondary titanium–alkyl complex **6** would prohibit the formation of $LiB(CH_2CH_2Ph)_4$ in the catalyzed reaction. Such selectivity is not without precedent, since phenylethene has shown a tendency to form benzylic metal–alkyl compounds in several transition metal catalyzed transformations.

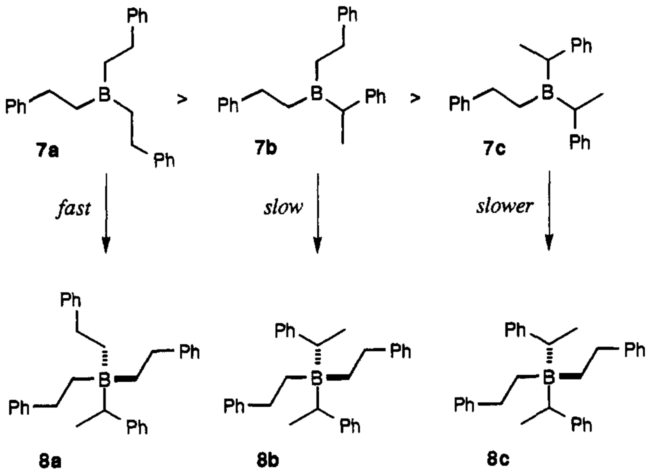


Figure 4. Expected relative reactivity of isomeric trialkylboranes **7a–c** toward alkyl transfer.

If, as we suggest in Scheme 2, the initial event in the titanium-promoted hydroboration of phenylethene is simply BH_3 hydroboration of the alkene, it is necessary to explain differences in the regioselectivities for the BH_3 and the Ti-promoted processes (Table 1, entries 1 and 3). Our explanation for this is as follows. The postulated alkyl transfer from titanium to boron would be expected to proceed faster for less-branched (and less-hindered) boranes, as depicted in Figure 4. This would proportionally decrease the amounts of the less-hindered boranes leaving relatively more borane precursors to secondary alcohols (*i.e.* **7b** and **7c**).

Higher yields and faster reaction rates for Isagawa's processes mediated by Cp_2TiCl_2, compared to the $Cp_2Ti(\mu\text{-}H)_2BH_2$-catalyzed reaction, can be attributed to the fast initial formation of BH_3 in the former case (reaction 1) leading to rapid initial hydroboration of alkene. After consumption of the BH_3 formed in reaction 1, the second stage of the reaction proceeds through the mechanism depicted in Scheme 2, and fewer turnovers of $Cp_2Ti(\mu\text{-}H)_2BH_2$ are needed to complete the reaction. Indeed, when the reaction of phenylethene with lithium borohydride in the presence of 0.1 equiv of Cp_2TiCl_2 was monitored by GC, fast initial consumption of alkene was observed (40% conversion in 1 h) followed by a slower reaction rate (90% conversion after 10 h).

The proposed model thus explains the formation of tetraalkylborates from the early stages of the catalytic process, the regioselectivity of hydroboration of phenylethene, and the slower rate of the reaction with stoichiometric $Cp_2Ti(\mu\text{-}H)_2BH_2$ and no borohydride. All steps in this mechanism have literature precedent, except we are unaware of any prior report of transmetalation from titanium to boron. Similar transfers from zirconium to boron are known, however.[50] We prefer the postulate presented above to alternatives involving catalyzed additions of trialkylborohydrides to phenylethene. Such a process would require simultaneous coordination of two cyclopentadienyl groups, an alkene, and a trialkylborohydride, and this seems improbable for steric reasons.

Titanium-Promoted Hydroborations of 1-Decene and β-Pinene. In some respects, different results were obtained for titanium-promoted hydroborations of 1-decene and β-pinene compared with those of phenylethene. Visually, the reaction of these alkenes are very similar, *i.e.* a gradual change from bright violet to deep

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(45) James, B. D.; Nanda, R. K.; Wallbridge, M. G. H. *Inorg. Chem.* **1967**, *6*, 1979.

(46) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263.

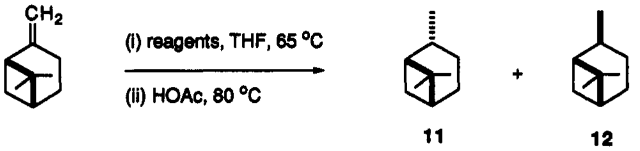
(47) Tajima, Y.; Kunioka, E. *J. Org. Chem.* **1968**, *33*, 1689.

(48) W. D. Bonds, J.; C. H. Brubaker, J.; Chandrasekaran, E. S.; Gibbons, C.; Grubbs, R. H.; Kroll, L. C. *J. Am. Chem. Soc.* **1975**, *97*, 2128.

(49) Grubbs, R. H.; Gibbons, C.; Kroll, L. C.; W. D. Bonds, J.; C. H. Brubaker, J. *J. Am. Chem. Soc.* **1973**, *95*, 2373.

(50) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880.

Table 2. Diastereoselective Hydroboration of β-Pinene Promoted by Titanium Complexes



entry	reagents, equiv	**11**:**12**	yield (%)	conversion (%)[a]	hydrogenation (%)[a]	time (h)
1	0.05 Cp_2TiBH_4 1.0 $LiBH_4$	77:23	62	94	35	25
2[19]	0.2 Cp_2TiCl_2 1.0 $NaBH_4$ 0.2 18-crown-6	74:26	59	*b*	*b*	*b*
3[c,d]	0.25 $NaBH_4$ 0.33 $BF_3{\cdot}OEt_2$	5:95	95	100	0	1

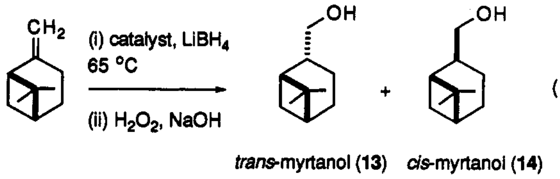
[a] By GC vs *trans*-decalin as internal standard. [b] No data reported.[19] [c] The reactive species is BH_3.[52] [d] At 25 °C.

purple with deposition of solid material on the wall of the reaction flask. However, the reactions of 1-decene and β-pinene with $Cp_2Ti(\mu\text{-}H)_2BH_2$ and borohydride were much slower than the corresponding transformation of phenylethene.

Attempts were made to characterize the products from the reaction of 1-decene using ^{11}B NMR. When the crude reaction mixture of 1-decene with 0.05 equiv of $Cp_2Ti(\mu\text{-}H)_2BH_2$ and 1.0 equiv of lithium borohydride was monitored after 36 h, only a very broad, nonresolved ^{11}B-resonance corresponding to borohydride (−41 ppm) was observed; this signal showed no coupling in the coupled spectrum indicative of exchange processes. Three additional minor signals emerged on treatment of the crude reaction mixture with $LiAlH_4$/DABCO: a quartet at −28.4 ppm, a triplet at −18.8 ppm, and a singlet at −16.9 ppm.[51] The BH_4^- signal at this stage is sharp and the coupling can be well resolved. Peaks corresponding to $RB(OEt)_2$ (31.8 ppm) and $R_2B(OEt)$ (54.2 ppm) were observed when the crude, incomplete reaction mixture after 20 h was quenched with ethanol instead of $LiAlH_4$/DABCO, implying that $LiBH_3R$ and $LiBH_2R_2$ and/or RBH_2 and R_2BH were present before ethanolysis.

Isagawa *et al.* reported that titanium-mediated hydroboration of β-pinene, and the corresponding BH_3 addition, followed by protonolysis gave different facial selectivities for the product alkanes (Table 2, entries 2 and 3; BH_3 in entry 3 was formed *in situ* from borohydride and boron trifluoride etherate).[19] Similar selectivities were observed when these reactions were repeated in our laboratories, but using isolated $Cp_2Ti(\mu\text{-}H)_2BH_2$ (entry 1) as "catalyst". However, during the titanium-mediated hydroborations of β-pinene we observed formation of significant quantities of pinane before protonolysis, presumably from metal-catalyzed hydrogenation processes. Furthermore, α-pinene produced from isomerization of β-pinene was also detected during the reaction (GC). Therefore, the alkane product distribution in entry 1 of Table 2 results from titanium catalyzed *hydrogenation* of α-pinene and β-pinene, and from metal-promoted *hydroboration* of these alkenes followed by protonolysis of the formed organoboranes.

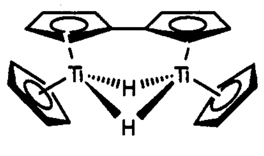
To distinguish between the hydrogenation and hydroboration processes we decided to oxidize the crude reaction mixtures from the titanium-mediated hydroborations of β-pinene; in this way organoboron compounds would be converted into alcohols, while the hydrogenation products would be unchanged. Surprisingly, the observed ratio of *cis*- and *trans*-myrtanol was 92:8 (reaction 10), *very close to the selectivity for* BH_3 *hydroboration of* β*-pinene.* We also hydroborated β-pinene under the conditions originally published (Cp_2TiCl_2:β-pinene:BH_4^- = 1:5:5, 65 °C) and oxidized the crude reaction mixture. Once more, the ratio of *cis*- and *trans*-myrtanol (94:6) was very similar to that for BH_3 hydroboration of β-pinene. The striking difference in the product ratios after protonolysis or oxidation of the crude reaction mixture suggests that isomerization of organoboron compounds during protonolysis in the presence of titanium complexes may occur.



(10)

catalyst	**13**:**14**
10 mol % Cp_2TiBH_4	9:91
20 mol % Cp_2TiCl_2	6:94

The proposed mechanism for the $Cp_2Ti(\mu\text{-}H)_2BH_2$-promoted hydroboration of phenylethene must be modified when 1-decene and β-pinene are substrates. Only trace amounts of tetraalkylborates were observed in experiments with these aliphatic alkenes, and the reactions were also more sluggish compared with phenylethene. There could be several reasons for these observations. Insertion of 1-decene or β-pinene into the titanium hydride bond of **5** might be very slow. However, since hydrogenation products (which also require insertions into titanium hydride bonds) were observed, the alkyl transfer from titanium to boron might be retarded instead. Consequently, we believe this decrease in reactivity of 1-decene (and other similar alkenes) compared with phenylethene probably reflects the electronic difference between alkyl- and aryl-substituted alkenes. Studies on titanocene catalyzed hydrogenation have shown that dicyclopentadienyl titanium hydrides readily dimerize to the catalytically inactive species **15** and related polymeric materials.[53-55] Therefore if alkene is not capable of insertion into the titanium hydride bond of **5**, dimerization will break the catalytic cycle. The products of the reactions of 1-decene and β-pinene could still be generated via BH_3 hydroboration, as in the first steps of the proposed mechanism for phenylethene (Scheme 2). Regeneration of the catalyst, however, is suppressed leading to decreased reaction rates for 1-decene and β-pinene.



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We propose that the borane products of the reactions of 1-decene and β-pinene are probably in equilibrium with borohydride and are not observable in the ^{11}B NMR spectra of the crude reaction mixtures. This equilibrium could explain the observation by Isagawa that products from titanium-promoted hydroboration of 2-octene do not isomerize at 150 °C (see background). Finally, the observed predominant monohydroboration of alkynes can be explained by the slow rate of BH_3 production in the presence of a large excess of alkyne. After the first hydroboration produces vinylboranes, these products may enter the equilibrium with lithium borohydride preventing further reaction.

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(51) The dialkylborohydride resonances giving doublet and triplet resonances in this ^{11}B NMR spectrum could be derived from alkyl transfer between trialkylborohydrides and AlH_3 (formed from the $LiAlH_4$), but this should have been suppressed by DABCO since DABCO·AlH_3 is formed under these conditions.

(52) Brown, H. C.; Murray, K. J.; Murray, L. J.; Snover, J. A.; Zweifel, G. *J. Am. Chem. Soc.* **1960**, *82*, 4233.

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(54) Davison, A.; Wreford, S. S. *J. Am. Chem. Soc.* **1974**, *96*, 3017.

(55) Bottrill, M.; Gavens, P. D.; McMeeking, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Ed.; Pergamon: New York, 1982; Vol. 3, pp 314.

Conclusion

This study addresses several key issues regarding titanium-catalyzed additions of borohydride to alkenes. First, $Cp_2Ti(\mu\text{-}H)_2BH_2$ promotes the addition of $LiBH_4$ to alkenes, but is not directly involved in the hydroboration step. Second, the products of hydroboration of phenylethene were shown to consist primarily of regioisomeric tetraalkylborates, and minor amounts of trialkylborohydrides were produced also. The resulting ratio of primary to secondary alcohols after oxidation of the crude reaction mixture is decreased, because the nonoxidizable tetraalkylborates are predominantly formed from less-branched trialkylboranes. A reaction mechanism is proposed that accommodates the observed characteristics for the titanium-promoted hydroboration of phenylethene.

Organoboranes are produced in titanium-mediated hydroboration of 1-decene and β-pinene. These products are involved in a dynamic equilibrium with lithium borohydride resulting in a mixture of alkylboranes and alkylborohydrides or in dimeric species. Tetraalkylborates are not formed to any significant extent for β-pinene and 1-decene. The organoboron products from titanium-promoted reaction of β-pinene produce the same ratio of diastereomeric alcohols after oxidation as BH_3 hydroboration.

This study illustrates the complexity of reactions of alkene with borohydride promoted by transition metal complexes. Genuine catalysis of hydroboration is hard to distinguish from metal-promoted formation of BH_3, followed by classical hydroboration.[56] Nevertheless, the exercise is important, since this distinction is critical with respect to applications of these reactions. Moreover, some characteristics of the titanium-mediated process are now apparent, and are potentially useful. For instance, new transformations involving titanium-to-boron alkyl transfer can now be seriously contemplated.

Experimental Section

General Procedures. High-field NMR-spectra were recorded on a Varian XL 200 (^{11}B at 64.2 MHz). Multiplicities in ^{11}B NMR are reported as (br) broad, (sh) sharp, (s) singlet, (d) doublet, (t) triplet, and (q) quartet. ^{11}B chemical shifts are reported in ppm relative to the external standard $BF_3{\cdot}OEt_2$ (0.00 ppm). Quartz NMR tubes for ^{11}B NMR and coaxial inserts were purchased from Wilmad Glass. ^{11}B NMR of crude reaction mixtures were taken with the coaxial insert charged with benzene-d_6 and $BF_3{\cdot}Et_2O$ for locking and reference purposes or after addition of a small amount of degassed, dry benzene-d_6 to the reaction mixture. Gas chromatography (GC) was performed on a Shimadzu GC-9A interfaced with an Apple Macintosh IIsi using a 50 m (007 methyl phenyl (5%) silicone, 0.25 mm i.d. 0.25 μm film thickness) fused silica capillary column (Quadrex 007-2-50-0.25F); figures obtained for crude reaction mixtures were calibrated by injection of stock solutions containing known amounts of the different products. THF and diethyl ether (Et_2O) were distilled immediately before use from sodium benzophenone ketyl. Alkenes were purchased from commercial suppliers and distilled prior to use. Solutions of $LiBH_4$ and $LiAlH_4$ in THF were purchased from Aldrich Chemical Co; titanocene dichloride was obtained from Strem Chemicals. $Cp_2Ti(\mu\text{-}H)_2BH_2$ was prepared from sodium borohydride and titanocene dichloride as described in the literature;[23] and the shiny purple/violet crystals were isolated in a dry box and stored at −35 °C.

General Procedure for Hydroborations Catalyzed by $Cp_2Ti(\mu\text{-}H)_2BH_2$. A Schlenk tube was charged with 19.4 mg (0.1 mmol; 0.05 equiv) of $Cp_2Ti(\mu\text{-}H)_2BH_2$ inside a dry box. The tube was transferred to a Schlenk line and 1.0 mL of THF was added under an atmosphere of Ar, followed by 2.0 mL of a 2.0 M solution of $LiBH_4$ in THF. The violet/purple solution was stirred at 25 °C for 10 min prior to the addition of alkene (2 mmol; 1 equiv) and a small amount of *trans*-decahydronaphthalene as internal standard. The tube was immersed in an oil bath kept at 65 °C, and the reaction mixture was stirred until the reaction was complete or conversion of starting material had ceased as monitored by GC versus internal standard. The reaction flask was cooled to 0 °C and 2 mL of ethanol was added followed by 2 mL of 3.0 M NaOH solution. After careful addition of 2 mL of 30% H_2O_2 (exothermic reaction and H_2 evolution), the oxidation mixture was stirred for 5–7 h, diluted with 50 mL diethyl ether, and washed with 20 mL of 1 M NaOH solution and 20 mL of saturated NH_4Cl solution. The organic fraction was dried over Na_2SO_4 and the solvent was removed at reduced pressure.

General Procedure of Quenching with DABCO/$LiAlH_4$. The crude hydroboration reaction mixture was cooled to 0 °C and a solution of DABCO (1 equiv with respect to the amount of boron present) in THF was added. After stirring for 15 min a solution of $LiAlH_4$ in THF (1.0 M; 1 equiv) was added dropwise. An exothermic reaction occurred when tricoordinate alkylboranes were present. The reaction was left at 25 °C to ensure complete conversion and the ^{11}B NMR of the reaction mixture was taken.

Preparation of $LiHB(CH_2CH_2Ph)_x(CHCH_3Ph)_{3-x}$. Styrene (3.1 g; 30 mmol) was placed in a 50-mL round-bottom flask purged with N_2. THF (20 mL) was added, the flask was cooled to 0 °C, and 1.0 mL of borane–dimethyl sulfide complex (10.0–10.2 M) was added dropwise. After stirring at 25 °C for 3 h the reaction mixture was cooled to 0 °C, and 1.12 g (10 mmol; 1 equiv) of DABCO in 5 mL of THF was added. To the colorless, clear solution was added 10.0 mL of a 1.0 M solution of $LiAlH_4$ in THF at 0 °C, leading to an slightly exothermic reaction with the formation of a milky white emulsion. The reaction mixture was left at 25 °C for 12 h: ^{11}B NMR (THF/benzene-d_6) δ −5.7 (d, $J_{B\text{-}H}$ = 81.4 Hz, minor), −9.7 (d, $J_{B\text{-}H}$ = 78.0 Hz, major), −13.5 (d, $J_{B\text{-}H}$ = 73.6 Hz, major).

Preparation of $LiB(CH_2CH_2Ph)_x(CHCH_3Ph)_{4-x}$. Styrene (16 mmol) was hydroborated with $BH_3{\cdot}THF$ as described above. A solution of 4 mmol (2-phenylethyl)lithium in 15 mL of diethyl ether/pentane, prepared according to literature procedures,[35,36] was added at −78 °C to the crude styrene hydroboration product. Two layers form and after warming to 25 °C the bottom layer was transferred to a NMR tube. ^{11}B NMR (THF/benzene-d_6) δ −12.5 (br s, minor), −14.6 (br s, minor), −16.5 (sh s, major).

Preparation of $LiB(CH_2CH_2Ph)_4$. A solution containing 50 mmol of (2-phenylethyl)lithium in 50 mL of diethyl ether/pentane was added at −78 °C to a solution of 10 mmol of $BF_3{\cdot}Et_2O$ in 5 mL of diethyl ether. The solution was allowed to warm to 25 °C and the progress of the reaction was followed by ^{11}B NMR. The peak at 0 ppm corresponding to $BF_3{\cdot}Et_2O$ is slowly transformed into $LiB(CH_2CH_2Ph)_4$ at −16.3 ppm (sh s).

Time-Dependence of $Cp_2Ti(\mu\text{-}H)_2BH_2$-Catalyzed Hydroboration of Phenylethene. A large Schlenk tube was charged with 784 mg (4 mmol; 0.1 equiv) of $Cp_2Ti(\mu\text{-}H)_2BH_2$ inside a dry box. The tube was transferred to a Schlenk line and 10.0 mL of THF was added under an atmosphere of Ar, followed by 20.0 mL of a 2.0 M solution of $LiBH_4$ (40 mmol; 1 equiv) in THF. The violet/purple solution was stirred at 25 °C for 10 min prior to the addition of 8.15 g of phenylethene (80 mmol; 2 equiv) and a small amount of *trans*-decahydronaphthalene as internal standard. The reaction mixture was analyzed by GC and the tube was immersed in an oil bath kept at 65 °C. At regular time intervals 2.0 mL was transferred from the reaction mixture to a 10 mm quartz NMR tube equipped with an insert containing $BF_3{\cdot}Et_2O$ as internal standard. A ^{11}B NMR spectrum and a GC trace was taken and the consumption of starting materials and production of tetraalkylboronates were determined versus the internal standards.

Homogeneity Test. To a Schlenk tube charged with 38 mg of $Cp_2Ti(\mu\text{-}H)_2BH_2$ was added 1.0 mL of a 2.0 M solution of lithium borohydride in THF and 3 mL of a solution of 208 mg (2.0 mmol; 1 equiv) of styrene and 40 mg of *trans*-decahydronaphthalene in THF. Half of the resulting purple/violet solution was transferred to another Schlenk tube charged with 1.0 g of triple distilled metallic mercury and both flasks were immersed in an oil bath kept at 65 °C. At certain time intervals the progress of both reactions were analyzed by GC. After completion of the reactions, both mixtures were oxidized as described above and the ratio of primary to secondary alcohol in the crude product was established by GC.

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