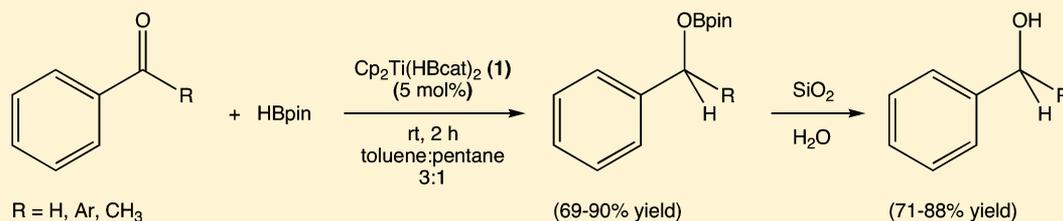


Titanocene(II)-Catalyzed Hydroboration of Carbonyl Compounds

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Supporting Information



ABSTRACT: Titanocene bis(catecholborane), $[\text{Cp}_2\text{Ti}(\text{HBcat})_2]$ (**1**), catalyzes the room-temperature hydroboration of carbonyl compounds by pinacolborane (HBpin) rapidly, cleanly, and chemoselectively. Aryl aldehydes and ketones produced alkoxy pinacolboronate esters in moderate to high yields in 2 h, and facile hydrolysis of alkoxy pinacolboronate esters over silica occurred cleanly to afford alcohols in good yields. Complex **1** demonstrated a preference for C=O bonds over C=C bonds in both conjugated and nonconjugated enones. Kinetic studies of the catalytic hydroboration of a series of acetophenones showed that electron-poor substrates undergo the reaction more quickly than electron-rich substrates. This result is consistent with the proposed mechanism, in which stronger π -acids should undergo C=O bond cleavage more readily. Computational studies using benzophenone and benzaldehyde showed that the hydroboration is spontaneous and likely proceeds via intermediates that are best described as Ti metallacycles whose structures are not significantly altered by substrate steric differences. This result indicates that similarities in the electronic properties of benzophenone and benzaldehyde supersede their steric differences in determining reaction outcomes.

INTRODUCTION

The hydroboration of carbonyl compounds is an efficient synthetic route to alcohols, and stoichiometric methods utilize boranes^{1–6} to synthesize borates, which are then hydrolyzed to alcohols. Metal-catalyzed hydroboration of ketones and aldehydes has also been reported, and examples include systems based on Ga,⁷ In,⁷ Mo(IV),⁸ Rh(I),⁹ Ru(II),¹⁰ Ti(IV),^{11–13} and Zn(II).¹⁴ Hill and co-workers very recently reported a Mg alkyl catalyst that efficiently hydroborates aldehydes and ketones.¹⁵ The Mg, Zn, and Ti systems exemplify metal-catalyzed hydroboration reactions that do not utilize costly and/or toxic mid to late transition metals. Similarly, we seek to provide carbonyl hydroboration catalysts based on earth-abundant, low-toxicity metals as cheaper and environmentally benign alternatives to more expensive rare-metal systems. In this regard, titanium is an attractive choice, because it is the fourth most abundant metal in the earth's crust (0.86% by weight) after aluminum, iron, and magnesium.¹⁶ The metal's abundance, coupled with its vast catalytic utility, make titanium a strong candidate for synthesizing versatile, cheap catalysts.^{17–19}

Examples of titanium-catalyzed hydroboration of carbonyls are limited to inorganic titanium(IV) oxides used in the catalytic hydroboration of carbonyls with catecholborane.^{11–13} Titanium-catalyzed hydroboration of carbonyls using pinacolborane,^{20–29} a reagent more robust than catecholborane, is yet unreported. Further, to our knowledge there have been no

reports of carbonyl hydroboration with titanocene catalysts, whose chiral ansa derivatives would be potentially useful in enantioselective catalysis.^{30–32} This application would be similar to asymmetric hydrosilylation of ketones, which has been well-studied and is a valuable route to chiral secondary alcohols.^{33–37}

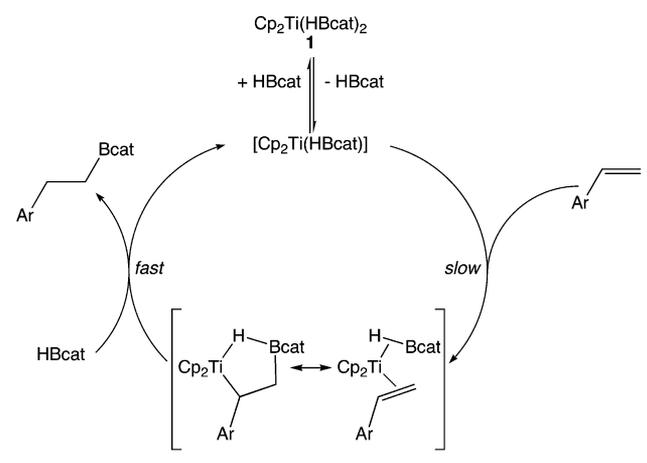
We have reported the use of titanocene(II) bis(catecholborane), $[\text{Cp}_2\text{Ti}(\text{HBcat})_2]$ (**1**), in the highly efficient hydroboration of vinylphosphines to yield phosphanyl-(organyl)boranes in short reaction times and under mild conditions.³⁸ This complex also performs rapid and high-yielding anti-Markovnikov hydroboration of vinylarenes.³⁹ The mechanism of catalytic hydroboration of vinylarenes by complex **1** is known to proceed via a two-step process (Scheme 1). Initial dissociation of catecholborane (HBcat) from complex **1** generates a mono(catecholborane) intermediate, the active catalyst, which undergoes vinylarene coordination in the rate-limiting step to generate an unobserved vinylarene–mono(catecholborane) intermediate. Rapid elimination of alkylcatecholboronate ester occurs with concomitant coordination of HBcat.

As part of our ongoing effort to explore the scope of the catalytic chemistry of complex **1**, we report on its hydroboration of carbonyl compounds with pinacolborane (HBpin)

Received: August 28, 2012

Published: December 19, 2012

Scheme 1. Mechanism of Catalytic Hydroboration of Alkenes by Complex 1



as the hydroborating agent. Kinetic and computational studies provide insight into the substrate preferences of complex **1**. The system reported herein is the first example of a titanium-based organometallic catalyst used for the hydroboration of carbonyl compounds.

RESULTS AND DISCUSSION

Titanocene bis(catecholborane), $[\text{Cp}_2\text{Ti}(\text{HBcat})_2]$ (**1**), catalyzes the hydroboration of aldehydes and ketones by pinacolborane (HBpin) selectively and rapidly at room temperature to afford alkoxy-pinacolboronate esters. Although catecholborane was previously used in vinylarene hydroborations by complex **1**,⁴⁰ pinacolborane afforded cleaner reactions in our system, likely because HBpin is a weaker π -acid than HBcat and thus has fewer side reactions.^{41–43}

We surveyed the utility of complex **1** with a range of carbonyl compounds, using HBpin as the sole hydroboration reagent. A representative set of substrates, products, and yields is presented in Table 1. Reactions were conducted by mixing benzene- d_6 solutions of the carbonyl substrate (1 equiv) and pinacolborane (1 equiv) with 5 mol % of complex **1** at room temperature. The resultant mixtures were analyzed by NMR spectroscopy over the course of 24 h. In all cases, new peaks were immediately observed in the ¹¹B NMR spectra between 21 and 23 ppm only, within the spectral region characteristic of alkoxyboronate esters.⁴⁴ Both aldehydes and ketones underwent catalysis cleanly without competing side reactions, and all reactions went to completion within 6 h.

Catalyzed reactions proceeded significantly more quickly than uncatalyzed reactions. For example, in the catalyzed reaction, hydroboration of 4'-chloroacetophenone yielded 88% alkoxy-pinacolboronate ester product after 2.5 h, while the uncatalyzed reaction yielded less than 5% of the hydroborated product over the same time period. Comparison with the only other two cases of metal-catalyzed hydroboration using HBpin shows that complex **1** is an improvement on Clark's Ru(II) catalyst¹⁰ but less efficient than Hill's Mg catalyst.¹⁵ For example, acetophenone yields 81% alkoxy-pinacolboronate ester product after 2.5 h at 20 °C with 5 mol % of complex **1** in C_6D_6 , while Clark's Ru(II) catalyst gave 50% product yield after 3 days at 70 °C with 4 mol % of catalyst in C_6D_6 .¹⁰ Hill's Mg catalyst yielded 94% of the same product after 4 h at 25 °C with 1 mol % catalyst loading in C_6D_6 .¹⁵

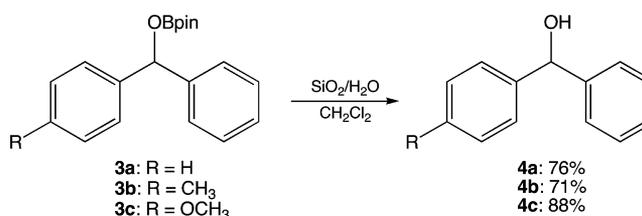
Table 1. Scope of Carbonyl Hydroboration Catalyzed by Complex 1^a

Substrate	Product	Yield
		NMR yield 86 %
		90% (3a)
2a: R = H	3a: R = H	Isolated yields 80 % (3a)
2b: R = CH ₃	3b: R = CH ₃	69 % (3b)
2c: R = OCH ₃	3c: R = OCH ₃	87 % (3c)
		NMR yields
		91% (R' = CF ₃)
		88% (R' = Cl)
		85% (R' = H)
		76% (R' = CH ₃)

^aAll reactions were performed using 5 mol % of complex **1**, at room temperature and in C_6D_6 solvent. NMR percent yields were determined via ¹H NMR spectroscopy of reaction mixtures after 2.5 h using Cp_2Fe as internal standard. Other conditions: [substrate] = 2.4×10^{-1} M; [pinacolborane] = 2.4×10^{-1} M; [complex **1**] = 1.2×10^{-2} M. Isolated products were obtained after 2 h of reaction time.

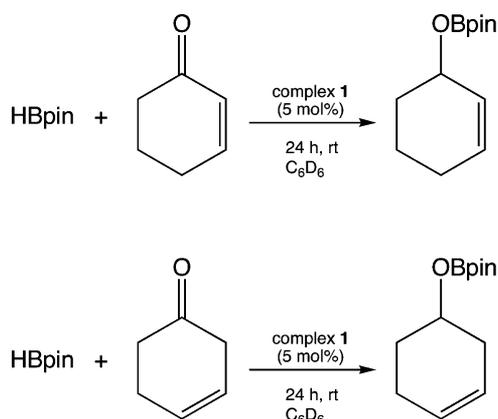
The hydroboration reaction, when performed in tandem with silica-promoted hydrolysis, furnishes alcohols in good yields. Hydroboration reactions were conducted by mixing toluene/pentane solutions of aryl ketones (1.4 M) with toluene/pentane solutions of pinacolborane (1.4 M) and then immediately adding the resultant mixture to solid complex **1** (5 mol %). Solutions were stirred at room temperature for 2 h, and completion of the reactions was confirmed by ¹¹B NMR spectroscopy. Alkoxy-pinacolboronate esters were precipitated from crude reaction mixtures by cooling to -30 °C overnight. Pure hydroborated products were collected in moderate to good yields as white crystalline solids. Secondary alcohols were isolated in good yields via silica-promoted hydrolysis of alkoxy-pinacolboronate esters. Hydrolysis was performed by passing solutions of the alkoxy-pinacolboronate esters in CH_2Cl_2 through a silica column, providing the benefit of hydrolysis and purification in a single step.¹⁰ Scheme 2 shows the results for a series of benzophenone substrates.

Catalyst selectivity for C=O vs C=C was compared using unsaturated ketone substrates (Scheme 3). Reactions were conducted by mixing benzene solutions of the carbonyl substrate and pinacolborane with 5 mol % of complex **1** at room temperature. The resultant mixtures were analyzed by ¹¹B NMR spectroscopy after 24 h. The ¹¹B NMR spectroscopic

Scheme 2. Alcohol Synthesis via Hydrolysis of Alkoxyboronate Esters^b

^bPercent yields are isolated yields.

Scheme 3. Hydroboration of Unsaturated Ketones Catalyzed by Complex 1



analysis of a reaction mixture of 3-cyclohexen-1-one and HBpin in the presence of complex **1** revealed a single resonance at 18.9 ppm in the region characteristic of alkoxyboronate esters, indicative of HBpin addition across C=O.⁴⁴ No peaks were observed between 29 and 39 ppm, within the region typical of alkylboronate esters, indicative of hydroboration across C=C.⁴⁴ Similarly, a reaction mixture of 2-cyclohexen-1-one and HBpin in the presence of complex **1** displayed a single peak at 18.3 ppm. The ¹H NMR spectrum of the reaction mixture revealed two new vinyl peaks at δ 5.89 and 5.64 in a 1:1 ratio, consistent with the formation of a 1,2-addition product. Thus, substrates bearing both conjugated and unconjugated C=C and C=O bonds exclusively added HBpin across the C=O bond, demonstrating the chemoselectivity of this system. This selectivity for the C=O bond of nonconjugated enones differs from the C=C bond preference by Wilkinson's catalyst reported by Nöth.⁴⁵ Further, 1,2-hydroboration of conjugated enones by complex **1** offers an alternative to the Evans/Fu 1,4-conjugate hydroborations of conjugated enones catalyzed by Rh(I).⁴⁶

The effects of carbonyl substrate electronic properties and steric properties on hydroboration catalyzed by complex **1** were investigated separately on a series of acetophenones and aryl carbonyls, respectively. To systematically investigate the effect of electronic properties, hydroboration rates of five para-substituted acetophenones were measured and compared. Benzene-*d*₆ solutions of the acetophenone substrate, pinacolborane, and ferrocene internal standard were added to preweighed complex **1** and ¹H NMR spectra of reaction mixtures acquired every 60 s for at least 3*t*_{1/2}. Concentrations of acetophenone reactant were determined by integration of aromatic protons relative to ferrocene in the ¹H NMR spectrum. Pinacolborane was used in 5-fold excess concentration for pseudo-first-order kinetic conditions. Linear first-order plots were obtained and used to determine the observed rate constants. A representative first-order linear plot for 4'-methylacetophenone is shown in Figure 1.

The data revealed that electron-poor ketones react more quickly than electron-rich ketones, suggesting that a process strongly influenced by electronics, such as π -bond cleavage, may be involved in the rate-limiting step of the reaction. The Hammett plot presented in Figure 2 illustrates the observed trend.

The effect of substrate sterics on hydroboration was also investigated by comparing the reactivity of two aryl carbonyls

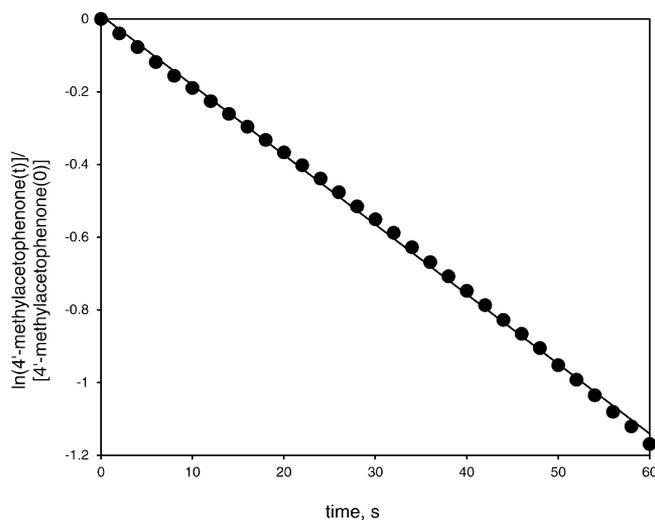


Figure 1. Representative linear first-order decay plot for hydroboration of 4'-methylacetophenone.

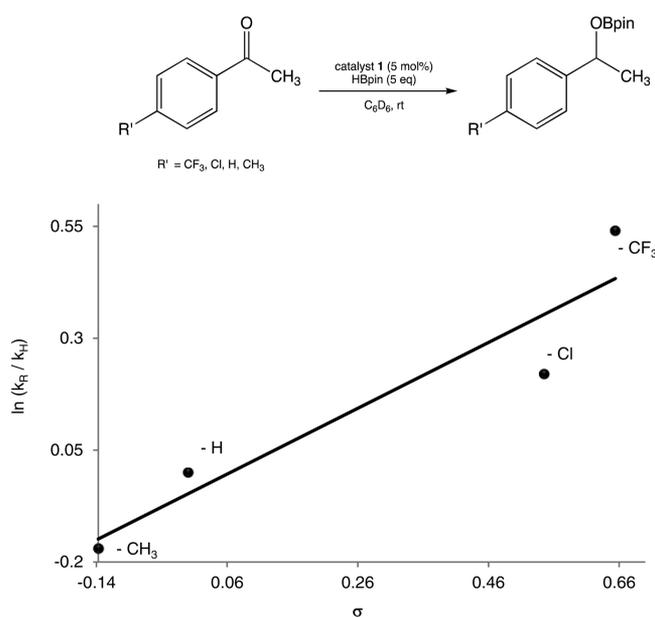
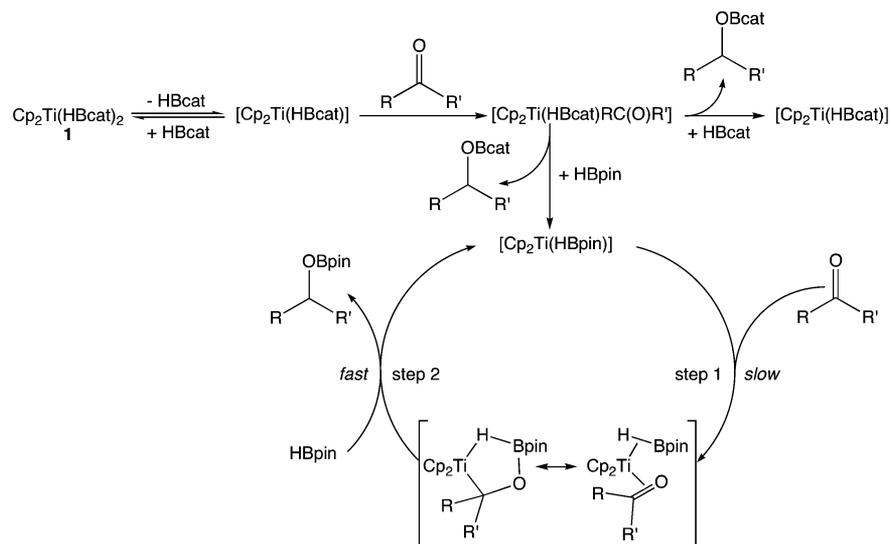


Figure 2. Hammett plot for the hydroboration of arylketones by complex **1** (5 mol %) at 20 °C. k_R = rate constant for hydroboration of 4'-substituted acetophenone; k_H = rate constant for hydroboration of acetophenone.

with similar electronic properties but dramatically different steric properties: benzophenone and benzaldehyde. Benzene-*d*₆ solutions of the carbonyl, pinacolborane (1 equiv), and ferrocene internal standard were added to preweighed complex **1**, and the reaction mixtures were analyzed by ¹H NMR spectroscopy at room temperature. Reactions were clean and provided hydroborated products exclusively; percent yields were equivalent to percent conversions. Surprisingly, despite the structural difference between the two compounds, the percent conversions of benzophenone (90%) and benzaldehyde (86%) were comparable after 2.5 h at room temperature (Table 1). This result suggests that steric properties may be less important than electronic properties in carbonyl hydroboration by our system.

A mechanism for the catalytic hydroboration of carbonyls by complex **1**, analogous to the reported vinylarene hydroboration

Scheme 4. Postulated Mechanism for Catalytic Hydroboration of Carbonyls by Complex 1



pathway (Scheme 1), is postulated in Scheme 4.³⁹ In the precatalytic step, the monocatecholborane intermediate ($[\text{Cp}_2\text{Ti}(\text{HBcat})]$) is formed via HBcat dissociation from complex 1. This intermediate then coordinates carbonyl and eliminates alkoxyatecholboronate ester with concomitant HBpin or HBcat coordination. Coordination by HBcat regenerates $[\text{Cp}_2\text{Ti}(\text{HBcat})]$, which again hydroborates the carbonyl to provide a second alkoxyatecholboronate ester molecule, thus furnishing a total of two catalytic equivalents of alkoxyatecholboronate ester. Coordination by HBpin yields $[\text{Cp}_2\text{Ti}(\text{HBpin})]$, the active catalyst, and the rest of the catalysis occurs with HBpin.

In the catalytic cycle proper, carbonyl substrate slowly coordinates $[\text{Cp}_2\text{Ti}(\text{HBpin})]$ (step 1), in agreement with our observation of first-order kinetics with respect to carbonyl. As with the vinylarene hydroboration mechanism pathway,³⁹ the intermediate generated in step 1 is most likely a resonance structure between a Ti(II) η^2 -carbonyl complex and a Ti(IV) metallacycle. Subsequent elimination of alkoxy-pinacolboronate ester product from the intermediate (step 2) occurs rapidly upon coordination of incoming pinacolborane.

In order to explain the observed trends in substrate reactivity, we investigated factors influencing the formation and stability of the unobserved Ti(II) η^2 -carbonyl/Ti(IV) metallacyclic intermediate. Soft titanium(II) should bind carbonyls, as it is well-known that transition-metal centers bind carbonyls in an η^2 fashion. The stability of the resultant complexes depends on the degree of metal–ligand back-donation, with the extent of back-donation regulated by the metal softness and/or ligand π -acidity.⁴⁷ For example, an early report by Erker et al. demonstrated that benzophenone binds zirconocene to form the isolable complex $\text{Cp}_2\text{Zr}(\eta^2\text{-Ph}(\text{CO})\text{Ph})$, stabilized by back-donation from the soft Zr(II) metal center.⁴⁸ In addition, Gladysz has shown that the Re(II) fluoro ketone complex $[\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\text{CH}_2\text{F}(\text{CO})\text{CH}_2\text{F})]^+$ is more stable than the analogous chloro ketone complex $[\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}(\text{CH}_2\text{ClCOCH}_2\text{Cl})]^+$, presumably due to the enhanced π -ligand acidity and back-donation in the former.⁴⁹

Computational studies provided insight into the relative importance of substrate electronic properties vs steric properties in the catalysis. The calculations optimized the structures of benzophenone and benzaldehyde in the gas phase and

compared the electronic and structural properties of the two compounds. The initial structures of both compounds were constructed with GaussView 5.0,⁵⁰ and the geometries of both compounds were optimized using the B3PW91 method from the Gaussian 09 package.⁵¹ The 6-31G(d,p) basis set was adopted in these computations. The atomic charges on the optimized structures of benzophenone and benzaldehyde were analyzed, and the negative charge was found to be highly localized on the carbonyl oxygen atom in both molecules.⁵² The net charge on benzophenone's carbonyl group was -0.113 , and that on benzaldehyde was -0.163 , indicating a slightly higher electron density in benzaldehyde. This result is consistent with the experimentally determined 86% conversion for the slightly more electron rich benzaldehyde vs 90% conversion for benzophenone. Although these values are close, they are consistent with the hypothesis that more electron rich substrates undergo the reaction less readily.

The relative energies of the frontier molecular orbitals of the two molecules further rationalize these findings, and Figure 3 depicts the orbital energies of both compounds. The LUMOs are recipients of metal electron density in the C=O bond cleavage process, and their energies are virtually identical (-1.80 eV in benzophenone and -1.81 eV in benzaldehyde),

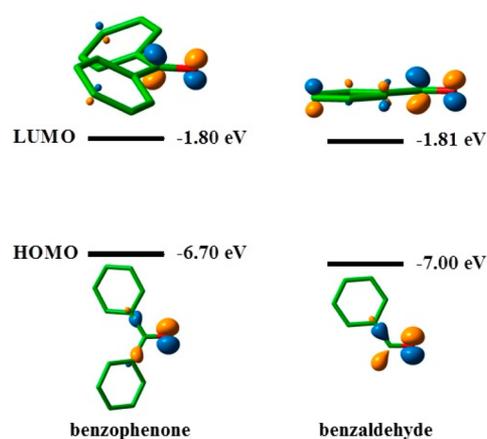


Figure 3. Frontier molecular orbital energies of benzophenone and benzaldehyde.

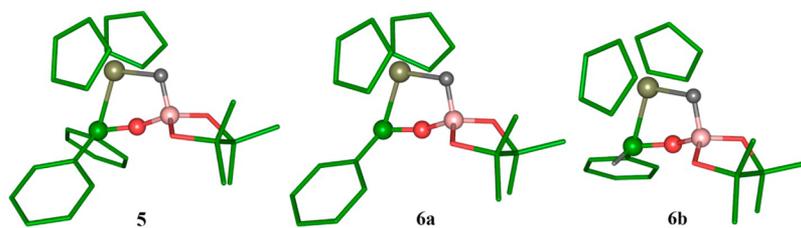


Figure 4. Optimized structures of $[\text{Cp}_2\text{Ti}(\text{HBpin})(\text{PhC}(\text{O})\text{Ph})]$ (**5**), $[\text{Cp}_2\text{Ti}(\text{HBpin})((R)\text{-HC}(\text{O})\text{Ph})]$ (**6a**), and $[\text{Cp}_2\text{Ti}(\text{HBpin})((S)\text{-HC}(\text{O})\text{Ph})]$ (**6b**).

demonstrating the similarity of the substrates' electrophilic nature.

Computations were conducted to determine possible structures for the intermediates generated from coordination of benzophenone and benzaldehyde to $[\text{Cp}_2\text{Ti}(\text{HBpin})]$. The B3PW91 method was able to reproduce experimental geometries of titanocene borane complexes⁵³ and was therefore adopted in this work. The LanL2DZ basis set was used for Ti, and the 6-31G(d,p) basis set was used for all the other atoms in geometry optimizations of all the complexes.

The optimized structures of the benzophenone complex $[\text{Cp}_2\text{Ti}(\text{HBpin})(\text{PhC}(\text{O})\text{Ph})]$ (**5**), the pro-*R* benzaldehyde complex $[\text{Cp}_2\text{Ti}(\text{HBpin})((R)\text{-HC}(\text{O})\text{Ph})]$ (**6a**), and the pro-*S* benzaldehyde complex $[\text{Cp}_2\text{Ti}(\text{HBpin})((S)\text{-HC}(\text{O})\text{Ph})]$ (**6b**) are shown in Figure 4, and the structural parameters of these complexes are given in Table 2.

Table 2. Optimized Geometries of $[\text{Cp}_2\text{Ti}(\text{HBpin})(\text{PhC}(\text{O})\text{Ph})]$ (5**), $[\text{Cp}_2\text{Ti}(\text{HBpin})((R)\text{-HC}(\text{O})\text{Ph})]$ (**6a**), and $[\text{Cp}_2\text{Ti}(\text{HBpin})((S)\text{-HC}(\text{O})\text{Ph})]$ (**6b**)**

bond distance (Å)/angle (deg)	$[\text{Cp}_2\text{Ti}(\text{HBpin})(\text{PhC}(\text{O})\text{Ph})]$ (5)	$[\text{Cp}_2\text{Ti}(\text{HBpin})((R)\text{-HC}(\text{O})\text{Ph})]$ (6a)	$[\text{Cp}_2\text{Ti}(\text{HBpin})((S)\text{-HC}(\text{O})\text{Ph})]$ (6b)
$R_{\text{Ti}-\text{C}}$	2.23	2.17	2.16
$R_{\text{Ti}-\text{B}}$	2.47	2.46	2.48
$R_{\text{C}-\text{O}}$	1.40	1.39	1.38
$R_{\text{O}-\text{B}}$	1.49	1.49	1.48
$R_{\text{B}-\text{H}}$	1.36	1.36	1.38
$R_{\text{H}-\text{Ti}}$	1.76	1.76	1.77
$\text{Ti}-\text{C}-\text{O}$	65.2	67.9	68.5
$\text{C}-\text{O}-\text{B}$	153.3	150.3	141.3
$\text{O}-\text{B}-\text{H}$	100.2	101.0	99.9
$\text{B}-\text{H}-\text{Ti}$	104.2	103.3	103.1
$\text{H}-\text{Ti}-\text{C}$	105.4	106.1	103.7

The data show that the calculated C–O bond distances in all the intermediates are between 1.38 and 1.40 Å and thus more closely resemble a C–O bond (1.43 Å) than a C=O bond (1.20 Å).⁵⁴ Indeed, the titanium(IV) complex $[\text{Cp}_2\text{Ti}(\text{PMe}_3)(\text{PhC}(\text{O})\text{Ph})]$, recently reported by Norton and co-workers to display a characteristic C–O single bond, has a C–O distance of 1.36 Å.⁵⁵ The calculated Ti–C bond lengths of 2.16–2.23 Å are also close to the crystallographically determined Ti–C bond length of 2.25 Å in Norton's Ti(IV) complex. The Ti–C bond distance is slightly longer in the benzophenone complex (**5**, 2.23 Å) than in the benzaldehyde complexes (**6a**, 2.17 Å; **6b**, 2.16 Å). This modest difference may be attributed to a more negative charge on the C=O group of benzaldehyde that may strengthen and shorten the Ti–C bond in **6a,b**. The B–H bonds (1.36–1.38 Å) are longer than the B–H bonds (1.25 Å) of HBcat in the σ -complex **1**,⁵⁶ while the B–O(carbonyl) bond

distances (1.48–1.49 Å) are slightly longer than typical B–O covalent bonds (1.36 Å).⁵⁴

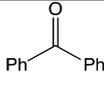
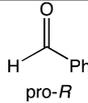
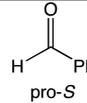
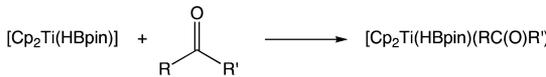
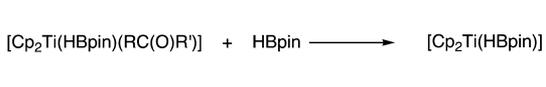
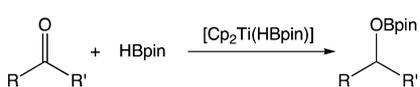
The Ti–H bonds (1.76–1.77 Å) are shorter than the Ti^{II}–H bond in $[\text{Cp}_2\text{Ti}(\eta^2\text{-Ph}_2\text{SiH}_2)(\text{PMe}_3)]$ (1.81 Å⁵⁸) and similar to the Ti^{III}–H bond distances in $[\text{Cp}_2\text{TiSiH}_2\text{Ph}]_2$ (1.76 Å⁵⁹) and $[\text{Cp}^*\{\text{C}_5\text{Me}_4\text{CH}_2(\text{C}_2\text{H}_3\text{MeN})\}\text{TiH}]$ (1.70 Å⁵⁷). The Ti–B bonds (2.46–2.48 Å) are slightly longer than that in σ -complex **1** (2.34 Å).⁵⁶ These data support the structure of intermediates **5** and **6a,b** as five-membered rings bearing a Ti metal center with a formal charge greater than +2 and are best described as resonance hybrids of a Ti(IV) metallacycle and a Ti(II) η^2 -carbonyl complex (Scheme 4). However, the intermediates may more closely resemble the metallacyclic contributor, because the C–O bond more closely resembles a single bond,⁵⁴ the Ti–C bond is similar to that in a crystallographically characterized Ti(IV) carbonyl complex,⁵⁵ and the Ti–B bond is longer than that in titanocene σ -complexes.⁵⁶

Free energy calculations for the catalytic hydroboration of benzophenone and benzaldehyde confirmed that, overall, reactions were spontaneous, indicating that the proposed intermediate structures were reasonable. The ΔG values of the overall reactions show that hydroboration of benzaldehyde is slightly favored over hydroboration of benzophenone (4 kcal/mol for pro-*R* benzaldehyde and 2.38 kcal/mol for pro-*S* benzaldehyde); the closeness of these values is in accord with the similarity of experimentally determined conversions. Computations on step 1 showed that coordination of $[\text{Cp}_2\text{Ti}(\text{HBpin})]$ by pro-*R* benzaldehyde to generate complex **6a** is 1.39 kcal/mol higher than coordination by pro-*S* benzaldehyde to form complex **6b**, indicating that **6a** is slightly less stable than **6b**. In step 2, formation of the hydroborated product from the *R* intermediate **6a** is favored over formation of the hydroborated product from the *S* intermediate **6b** by 3.01 kcal/mol. Overall, the reaction with pro-*R* benzaldehyde is 1.62 kcal/mol more favorable than that with pro-*S* benzaldehyde, suggesting that the benzaldehyde complex may favor an *R* configuration during the catalytic cycle.

CONCLUSION

The catalytic hydroboration of carbonyls by complex **1** is influenced strongly by substrate electronic factors and, to a marginal extent, by their steric factors. All acetophenone substrates had similar steric properties at C=O but differed in electronic properties at this same site; any difference in their hydroboration rates can be attributed exclusively to differences in electronic properties. We found that more electron poor carbonyls underwent reactions more quickly, perhaps because more electron poor carbonyls experience greater metal–carbonyl π^* -back-donation and, consequently, more facile C=O bond cleavage. Thus, electron-poor carbonyls may

Table 3. Free Energies of Reactions (kcal/mol) in the Catalytic Cycle for the Hydroboration of Benzaldehyde and Benzophenone

Reactions			
Step 1: 	5.38	-7.74	-9.13
Step 2: 	-27.52	-18.40	-15.39
Net catalytic reaction: 	-22.14	-26.14	-24.52

more easily generate thermodynamically accessible intermediates.

Computational studies on the intermediates generated in the hydroboration of benzophenone and benzaldehyde indicate a metallacyclic configuration, which is a resonance hybrid structure of the metallacyclic Ti(IV) and the Ti(II) η^2 -carbonyl contributors. The structure of the intermediates does not appear to be significantly affected by the steric differences between benzaldehyde and benzophenone. Calculations showed that benzophenone and benzaldehyde have similar electronic properties at C–O and that ΔG values for the two overall reactions were similar. We conclude that, in this reaction, the electronic similarities in benzaldehyde and benzophenone override their steric differences, and the two substrates behave virtually identically. Future studies will focus on further extending the scope of the catalysis to other heteroatomic substrates.

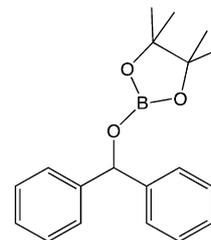
EXPERIMENTAL SECTION

General Procedures. Unless otherwise noted, all experiments were performed using oven-dried or flamed glassware and conducted using standard Schlenk techniques or in a VAC OmniLab System 37897 inert-atmosphere glovebox (Vacuum Atmospheres Co., Hawthorne, CA) equipped with an oxygen sensor (working at <1 ppm) and a refrigeration unit ($-30\text{ }^\circ\text{C}$).

Instrumentation. ^1H , ^{13}C , and ^{11}B NMR spectra were obtained on a JEOL-ECS 400 MHz NMR spectrometer operating at 399.78, 100.52, and 128.27 MHz, respectively, at $19.2\text{ }^\circ\text{C}$. All ^{13}C and ^{11}B NMR signals reported were decoupled from proton resonances. ^1H NMR spectra were recorded relative to residual protiated solvent. ^{11}B NMR and ^{31}P NMR spectra were recorded in units of parts per million relative to $\text{BH}_3\cdot\text{Et}_2\text{O}$ and 85% H_3PO_4 , respectively, as external standards.

Materials. Unless specified otherwise, all reagents were purchased from commercial suppliers and used without further purification. Titanocene bis(catecholborane), $[\text{Cp}_2\text{Ti}(\text{HBcat})_2]$ (**1**), was prepared via the literature procedure.³⁹ All protiated solvents were purified and distilled from VAC solvent purifier systems, sparging with nitrogen gas. Deuterated solvents were refluxed and distilled by vacuum transfer from purple solutions containing sodium benzophenone. Silica gel (30–200 mesh) was used for hydrolysis of boronate ester products.

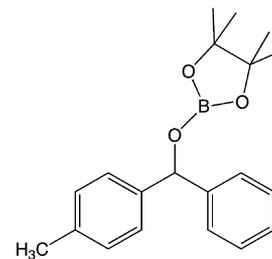
Synthesis of 2-(Diphenylmethoxy)pinacolborane (**4a**).



A vial was charged with benzophenone (1.00 g, 5.50 mmol) and a 3/1 toluene/pentane mixture ($\sim 4\text{ mL}$), forming a clear colorless solution. Into a separate vial was weighed 5 mol % of $\text{Cp}_2\text{Ti}(\text{HBcat})_2$ (**1**; 115 mg, 0.275 mmol), and in this vial was added a solution of pinacolborane (800 μL , 5.50 mmol) in toluene ($\sim 2\text{ mL}$). The benzophenone solution was added by pipet to the vial containing the catalyst and pinacolborane, and the resultant mixture was stirred for 2 h at room temperature. After this time period, the reaction mixture was layered with pentane ($\sim 2\text{ mL}$) and stored for 3 h at $-30\text{ }^\circ\text{C}$. The hydroboration product precipitated from solution as a white solid. The product was collected via vacuum filtration using a precooled frit, washed with cold pentane, and allowed to dry. A white flaky solid was collected (1.36 g, 4.40 mmol, 80% yield).

^1H NMR (C_6D_6 , 400 MHz): δ 7.45 (d, $J = 6.7\text{ Hz}$, 2H), δ 7.08 (t, $J = 6.8\text{ Hz}$, 2H), δ 6.99 (t, $J = 7.3\text{ Hz}$, 1H), δ 6.44 (s, 1H), δ 0.967 (s, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz): δ 143.7, 128.4, 127.4, 126.8, 82.6, 78.3, 24.4. $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6 , 128 MHz): 22.5 (s).

Synthesis of 2-(1-(4-Methylphenyl)-1-phenylmethoxy)-pinacolborane (**4b**).

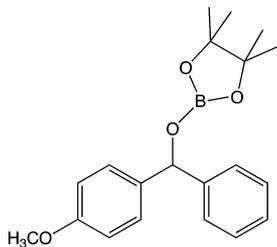


The procedure for the synthesis of 1,1-diphenylmethanol was repeated using 4-methylbenzophenone (1.00 g, 5.10 mmol) instead of benzophenone. The product was collected as a white flaky solid (1.14 g, 3.52 mmol, 69% yield).

^1H NMR (C_6D_6 , 400 MHz): δ 7.48 (d, $J = 8.0\text{ Hz}$, 2H), 7.39 (d, $J = 4.0\text{ Hz}$, 2H), 7.10 (t, $J = 8.0\text{ Hz}$, 2H), 7.00 (t, $J = 4.0\text{ Hz}$, 1H), 6.92 (d,

$J = 8.0$ Hz, 2H), 6.46 (s, 1H), 2.03 (s, 12 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz): 140.9, 136.7, 129.1, 128.4, 128.0, 127.7, 127.3, 126.8, 126.7, 82.6, 78.3, 24.4, 20.8. $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6 , 128 MHz): 21.9 (s).

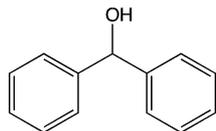
Synthesis of 2-(1-(4-Methoxyphenyl)-1-phenylmethoxy)pinacolborane (4c).



The procedure for the synthesis of 1,1-diphenylmethanol was repeated using 4-methoxybenzophenone (1.0 g, 4.71 mmol) instead of benzophenone. The product was collected as a white flaky solid (1.49 g, 4.10 mmol, 87% yield).

^1H NMR (C_6D_6 , 400 MHz): δ 7.48 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 12$ Hz, 2H), 7.12 (t, $J = 8.0$ Hz, 2H), 7.02 (t, $J = 8.0$ Hz, 1H), 6.70 (d, $J = 12$ Hz, 2 H), 6.43 (s, 1H), 3.23 (s, 3H), 0.99 (s, 6H), 0.98 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz): δ 158.9, 143.4, 135.6, 128.3, 128.0, 127.3, 126.4, 113.7, 83.0, 55.3, 31.0, 24.7. $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6 , 128 MHz): 21.5 (s).

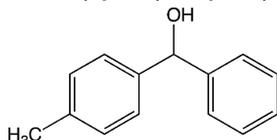
Synthesis of 1,1-Diphenylmethanol (5a).



On the laboratory bench in air, 2-(diphenylmethoxy)pinacolborane (0.577 g, 1.86 mmol) was dissolved in a vial with CH_2Cl_2 (~4 mL) and the solution passed through a silica plug. A clear colorless solution was collected and excess solvent removed via rotary evaporation. A white powdery solid was collected (0.260 g, 1.41 mmol, 76% yield).

^1H NMR (C_6D_6 , 400 MHz): δ 7.35 (m, 8H), 7.26 (m, 2H), 5.83 (d, $J = 4$ Hz, 1 H), 2.26 (d, $J = 4$ Hz, 1 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz): δ 143.9, 77.5, 77.2, 76.7, 76.4.

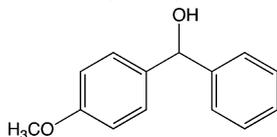
Synthesis of 1-(4-Methylphenyl)-1-phenylmethanol (5b).



The procedure for the synthesis of 1,1-diphenylmethanol was followed using 2-(1-(4-methylphenyl)-1-phenylmethoxy)pinacolborane (0.267 g, 0.822 mmol) instead of 2-(diphenylmethoxy)pinacolborane, and 1-(4-methylphenyl)-1-phenylmethanol formed as a colorless oil, which subsequently solidified to a white powdery solid after 12 h at room temperature (0.116 g, 0.584 mmol, 71% yield).

^1H NMR (C_6D_6 , 400 MHz): δ 7.17 (m, 4H), 7.08 (m, 3H), 6.98 (d, $J = 7.6$ Hz), 5.63 (d, $J = 1.8$ Hz, 1H), 2.17 (s, 3H), 2.08 (d, $J = 1.8$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz): δ 114.1, 141.2, 137.3, 129.3, 128.6, 127.6, 126.7, 126.6, 76.1, 21.3.

Synthesis of 1-(4-Methoxyphenyl)-1-phenylmethanol (5c).



The procedure for the synthesis of 1,1-diphenylmethanol was followed using 2-(1-(4-methoxyphenyl)-1-phenylmethoxy)pinacolborane (0.646 g, 1.89 mmol) instead of 2-(diphenylmethoxy)pinacolborane, and 1-(4-methoxyphenyl)-1-phenylmethanol formed as a colorless oil, which subsequently solidified to a white translucent solid after 12 h at room temperature (0.365 g, 1.66 mmol, 88% yield).

^1H NMR (C_6D_6 , 400 MHz): δ 7.34 (m, 4H), 7.26 (m, 3H), 6.85 (d, $J = 8.7$ Hz, 2H), 5.81 (d, $J = 2.2$ Hz, 1H), 3.77 (s, 3H), 2.33 (d, $J = 3.2$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100 MHz): δ 159.1, 144.1, 136.3, 126.5, 113.9, 77.5, 77.2, 76.9, 55.4.

Hydroboration of Acetophenone by Pinacolborane Catalyzed by Complex 1. A vial was charged with acetophenone (56 μL , 0.478 mmol) in C_6D_6 (1 mL), and to the resultant solution were added pinacolborane (69 μL , 0.478 mmol) and 200 μL of a 0.645 M solution of Cp_2Fe in C_6D_6 (internal standard). The resultant mixture was transferred into a vial containing preweighed 5 mol % of complex 1 (10 mg, 0.00239 mg) and stirred at room temperature. The resultant mixture was analyzed by NMR spectroscopy after 24 h. NMR yields were determined by measuring the integrals of the product methyl peaks or aromatic peaks and the cyclopentadienyl peaks of the internal standard.

^1H NMR (C_6D_6 , 400 MHz): δ 7.35 (d, $J = 7.3$ Hz, 2H), 7.13 (t, $J = 7.8$ Hz, 2H), 7.03 (t, $J = 7.3$ Hz, 1H), 5.40 (q, $J = 6.4$ Hz, 1H), 1.44 (d, $J = 6.4$ Hz, 3H), 1.00 (s, 6H), 1.01 (s, 6H). $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6): δ 25.8 (s).

Hydroboration of 4'-Chloroacetophenone by Pinacolborane Catalyzed by Complex 1. A procedure identical with that described for acetophenone was repeated using 4-chloroacetophenone (62 μL , 0.478 mmol). ^1H NMR (C_6D_6): δ 7.04 (s, 4H), 5.22 (q, $J = 6.4$ Hz, 1H), 1.32 (d, $J = 6.4$ Hz, 3H), 1.00 (s, 6H), 1.01 (s, 6H). $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6): δ 21.6 (s).

Hydroboration of 4'-Methylacetophenone by Pinacolborane Catalyzed by Complex 1. A procedure identical with that described for acetophenone was repeated using 4-methylacetophenone (64 μL , 0.478 mmol). ^1H NMR (C_6D_6): δ 7.30 (d, $J = 7.8$ Hz, 2H), 6.97 (d, $J = 7.8$ Hz, 2H), 5.42 (q, $J = 6.4$ Hz, 1H), 2.10 (s, 3H), 1.48 (d, $J = 6.4$ Hz, 3H), 1.00 (s, 6H), 1.02 (s, 6H). $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6): δ 19.0 (s).

Hydroboration of 4'-(Trifluoromethyl)acetophenone by Pinacolborane Catalyzed by Complex 1. A procedure identical with that described for acetophenone was repeated using 4-methoxyacetophenone (49 μL , 0.478 mmol). ^1H NMR (C_6D_6): δ 7.30 (d, $J = 8.2$ Hz, 2H), 7.10 (d, $J = 8.2$ Hz, 2H), 5.26 (q, $J = 6.4$ Hz, 1H), 1.30 (d, $J = 6.4$ Hz, 3H), 0.985 (s, 6H), 1.02 (s, 6H). $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6): δ 20.6 (s).

Hydroboration of 2-Cyclohexen-1-one by Pinacolborane Catalyzed by Complex 1. A vial was charged with 2-cyclohexen-1-one (46 μL , 0.478 mmol) in C_6D_6 (1 mL), and to the resultant solution was added pinacolborane (69 μL , 0.478 mmol). The resultant mixture was transferred into a vial containing preweighed 5 mol % of complex 1 (10 mg, 0.00239 mg), stirred at room temperature, and analyzed spectroscopically after 90 min. ^1H NMR (C_6D_6): δ 5.89 (m, 1H), 5.64 (m, 1H), 4.76 (m, 1H), 2.17 (m, 2H), 1.63 (m, 2H), 1.39 (m, 2H), 1.00 (s, 12H). $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6): δ 18.3 (s).

Kinetic Studies of Carbonyl Hydroboration Catalyzed by Complex 1. A vial was charged with acetophenone (56 μL , 0.478 mmol) in C_6D_6 (2 mL), and to the resultant solution were added 5 equiv of pinacolborane (345 μL , 2.39 mmol) and 200 μL of a 0.645 M solution of Cp_2Fe in C_6D_6 (internal standard). The resultant mixture was transferred into a vial containing preweighed 5 mol % of complex 1 (10 mg, 0.00239 mg) then transferred into an NMR tube; the tube was then shaken to dissolve all solids. The NMR tube was loaded into the NMR spectrometer quickly, and single-pulse experiments were performed every 30 s over at least 3 half-lives using an automated program. Rate measurements were performed by measuring the integrals of the product methyl peaks or aromatic peaks and the cyclopentadienyl peaks of the internal standard. Identical experiments were performed using 4-chloro-, 4-methyl-, and 4-methoxyacetophenones.

Computational Details. The initial structures of benzophenone, benzaldehyde, HBpin, $\text{Cp}_2\text{Ti}(\text{HBpin})$, $[\text{Cp}_2\text{Ti}(\text{HBpin})(\text{PhC}(\text{O})\text{Ph})]$ (5), $[\text{Cp}_2\text{Ti}(\text{HBpin})(\text{HC}(\text{O})\text{Ph})]$ (6a,b), and hydroborated products were all built using GaussView 5.0.⁵⁰ All the calculations were carried out using the Gaussian 09 package.⁵¹ Since the B3PW91 method was able to reproduce the experimental geometries of titanocene borane complexes,⁵³ it was adopted in this computational study. The 6-

31G(d,p) basis set was employed in optimizing the geometries of benzophenone, benzaldehyde, HBpin, and the final products. For Cp₂Ti(HBpin) and complexes **5** and **6a,b**, the LanL2DZ basis set was used for Ti, and the 6-31G(d,p) basis set was used for all the other atoms in geometry optimizations.

■ ASSOCIATED CONTENT

Supporting Information

Text, a figure, and tables giving details of the computations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by a Cottrell Science Grant Award (CCSA 7820) from Research Corp.

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■ NOTE ADDED AFTER ASAP PUBLICATION

In the version of this paper published on December 19, 2012, Tables 1 and 3 had some missing data. The version of this paper that appears as of December 20, 2012, is correct.