

# Mechanistic Studies of Titanocene-Catalyzed Alkene and Alkyne Hydroboration: Borane Complexes as Catalytic Intermediates

John F. Hartwig\* and Clare N. Muhoro

Department of Chemistry, Yale University, P.O. Box 208107,  
New Haven, Connecticut 06520-8107

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The bis(borane) complex  $\text{Cp}_2\text{Ti}(\text{HBcat}')_2$  is a highly active catalyst for the hydroboration of vinylarenes. We provide a detailed mechanistic analysis of this hydroboration process and of the hydroboration of alkynes catalyzed by titanocene dicarbonyl. The hydroboration of alkynes showed a reaction rate that was first order in the concentration of alkyne, inverse second order in the concentration of carbon monoxide, and first order in the concentration of borane. These data are consistent with a mechanism in which two equilibria involving  $\text{Cp}_2\text{Ti}(\text{CO})(\text{PhCCPh})$  generate the alkyne borane complex  $\text{Cp}_2\text{Ti}(\text{HBcat}')(\text{PhCCPh})$ , which forms the hydroboration product. The hydroboration of alkenes catalyzed by the bis(borane) complex  $\text{Cp}_2\text{Ti}(\text{HBcat}')_2$  involves the similar intermediate  $\text{Cp}_2\text{Ti}(\text{CO})(\text{RCH}=\text{CCH}_2)$ , containing a coordinated alkene, rather than alkyne. The catalytic process for alkene hydroboration is inverse first order in borane and first order in alkene, indicating that the reaction occurs by reversible dissociation of borane and coordination of alkene to form an alkene borane complex that undergoes elimination of alkylboronate ester. Reactions of this complex that compete with the production of alkylboronate ester include the formation of vinylboronate esters, presumably by  $\beta$ -hydrogen elimination of the intermediate complex formed by addition of alkene to coordinated borane. This  $\beta$ -hydrogen elimination pathway was suppressed by using excess catecholborane.

## Introduction

Transition-metal complexes catalyze the addition of catecholborane to alkenes and alkynes with enhanced rates and altered chemo-<sup>1</sup>, regio-<sup>2–6</sup> diastereo-<sup>5–10</sup> and enantioselectivities<sup>4,11–14</sup> relative to the uncatalyzed transformations.<sup>15,16</sup> Since Wilkinson's catalyst was first reported by Männig and Nöth<sup>1</sup> to promote the addition of catecholborane to alkenes, other late-transition-metal systems have been investigated.<sup>2,12,13,17–21</sup> Mechanistic studies have shown that Rh(I) catalysts promote the

addition of catecholborane to alkenes by a pathway involving initial oxidative addition of catecholborane to rhodium, followed by alkene migratory insertion and reductive elimination of the hydroborated product.<sup>22,23</sup> These borane additions are often complicated by side reactions such as  $\beta$ -hydride elimination to give vinylboronate esters and decomposition of catecholborane to diborane and hydrogen. The diborane formed by the latter process produces trialkylborane products, with selectivity that is independent of the catalyst.<sup>24–27</sup>

Early-transition-metal-catalyzed hydroborations have been less well studied. Lanthanide-catalyzed hydroboration of alkenes has been reported,<sup>28–30</sup> and a mechanism that is distinct from those of Rh(I) complexes has

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been proposed.<sup>28</sup> Olefin insertion into the lanthanide–hydride bond is well known, and this step was suggested to be followed by a  $\sigma$ -bond metathesis to provide anti-Markovnikov alkylboronate ester products. Our group recently reported that titanocene dimethyl is an efficient catalyst for the hydroboration of alkenes and that titanocene dicarbonyl catalyzes the hydroboration of alkynes.<sup>31</sup> Sneddon<sup>32</sup> has applied these results to the development of a process to form monoalkyldecaboranes.

Extensive studies by Burgess et al. have shown that previous titanium systems promoted hydroboration by decomposing catecholborane to diborane, which was responsible for hydroboration.<sup>24</sup> Some hydroboration catalysis with group IV complexes has been reported by Teuben et al., but low activity and borane decomposition were observed.<sup>30</sup> Subsequent studies<sup>31</sup> with pure dimethyltitanocene, however, showed that no trialkylboronate esters were formed, indicating that titanocene dimethyl did catalyze hydroboration and did not simply catalyze decomposition of catecholborane to diborane.

The catalytic hydroboration of alkynes with catecholborane has received less attention than the addition of this borane to alkenes<sup>21,23</sup> or the addition of polyboranes to alkynes,<sup>33–36</sup> even though the metal-catalyzed chemistry can induce mild and selective monoadditions to alkynes to produce vinylboronate esters that are useful in Suzuki cross-coupling chemistry.<sup>37</sup> Few alkyne hydroboration catalysts have been reported, and most of them are based on late-transition-metal systems.<sup>18–20,38,39</sup> Recently, we reported that  $\text{Cp}_2\text{Ti}(\text{CO})_2$  (**1**) catalyzes the hydroboration of alkynes without borane decomposition.<sup>31</sup> Srebnik et al. also reported an early-transition-metal system in which Schwartz's reagent ( $\text{Cp}_2\text{ZrHCl}$ ) catalyzes the hydroboration of alkynes by pinacolborane with excellent yields and selectivities.<sup>40</sup> Srebnik's system presumably operates by alkyne insertion and  $\sigma$ -bond metathesis, the same pathway as the lanthanide-catalyzed alkene hydroboration.

Preliminary mechanistic investigations on the catalytic hydroboration by  $\text{Cp}_2\text{TiMe}_2$  led to the discovery of the titanocene bis(borane)  $\sigma$  complex  $\text{Cp}_2\text{Ti}(\text{HBcat})_2$ .<sup>41</sup> This compound was formed from the reaction of titanocene dimethyl with excess catecholborane. Because no reaction was observed between titanocene dimethyl and alkenes at the temperature of the catalysis, we suspected that the bis(borane) complex was the active catalyst in the hydroboration of alkenes by titanocene dimethyl. Indeed, we report that hydroboration reactions catalyzed by titanocene bis(borane) complexes are

**Table 1. Hydroboration of Alkenes by 4-Methylcatecholborane Catalyzed by Bis(borane) Complex **2**<sup>a</sup>**

Substrate	Catalyst	cond.	products	yields (%)
	<b>2</b>	10 min 25 °C		90
	$\text{Cp}_2\text{TiMe}_2$	10 h 25 °C		96
	<b>2</b>	10 min 25 °C		100
	$\text{Cp}_2\text{TiMe}_2$	10 h 25 °C		96

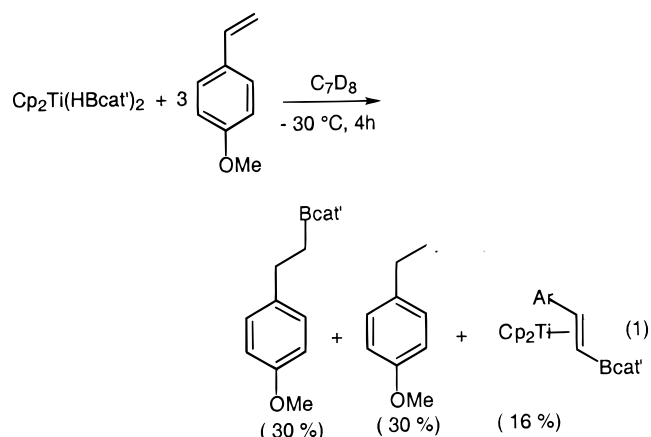
<sup>a</sup> 10 mol % catalyst used. Reactions were run in  $\text{C}_6\text{D}_6$  solvent, and yields were determined by  $^1\text{H}$  NMR spectroscopy with an internal standard.

faster than those catalyzed by titanocene dimethyl. Further, kinetic studies support the bis(borane) complex as the active catalyst. In addition to a brief presentation of the catalytic chemistry of  $\text{Cp}_2\text{Ti}(\text{HBcat}')_2$  (**2**), we report an extensive kinetic study of the catalysis by both **1** and **2** that supports reaction mechanisms that are distinct from those of either Rh(I) or other early-transition-metal-catalyzed hydroborations. Several types of monoborane Ti(II) complexes are intermediates.

## Results

**Hydroborations Catalyzed by  $\text{Cp}_2\text{Ti}(\text{HBcat}-4-t\text{-Bu})_2$  (**2**).** A comparison of the activity of **2** and  $\text{Cp}_2\text{TiMe}_2$  is summarized in Table 1. Indene and *p*-methoxystyrene gave a 95–100% yield of hydroborated product in only 10 min at room temperature—a rate that is much faster than those of the 10 h reactions catalyzed by  $\text{Cp}_2\text{TiMe}_2$ . Anti-Markovnikov products were formed exclusively in the reactions with indene and styrenes. The regiochemistry with vinylarenes is in contrast with that of most Rh(I)-catalyzed vinylarene hydroborations.<sup>1</sup>

**Mechanistic Studies on the Hydroboration of Alkenes Catalyzed by **2**.** Product compositions of reactions run with stoichiometric and catalytic quantities of **2** were different, and the higher ratio of HBcat' to catalyst seemed to be responsible for the different selectivity. We were initially surprised to observe that the reaction of complex **2** with *p*-methoxystyrene in the absence of HBcat' (HBcat' =  $\text{HBO}_2\text{C}_6\text{H}_4-4-t\text{-Bu}$ ) gave arylboronate ester in only 30% yield, *p*-(methoxyethyl)-benzene in 30% yield, and the titanocene vinylboronate ester complex  $\text{Cp}_2\text{Ti}(\text{cat}'\text{BCH}=\text{CHAr})$  in 16% yield (eq 1). The unsubstituted vinylboronate ester complex was



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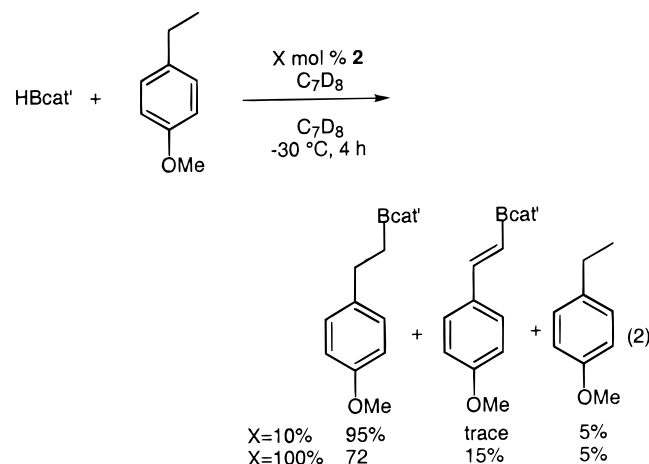
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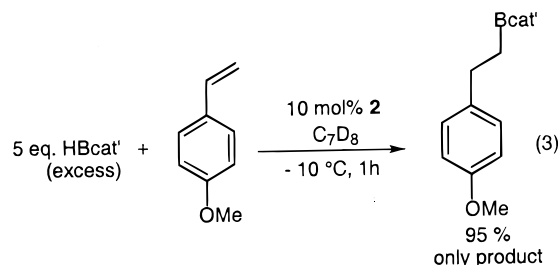
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independently prepared and fully characterized by the reaction of  $\text{Cp}_2\text{Ti}(\text{HBcat})_2$  with phenylacetylene. The reaction of equimolar quantities of **2** and *p*-methoxystyrene in the presence of  $\text{HBcat}'$  formed the arylboronate ester in a higher 72% yield, vinylboronate ester in 15% yield, and *p*-(methoxyethyl)benzene in 5% yield (eq 2). In contrast, the catalytic reactions produced only



trace amounts of hydrogenated product when equimolar proportions of alkene and  $\text{HBcat}'$  were used. For example, reaction of *p*-methoxystyrene with  $\text{HBcat}'$  in the presence of 10 mol % of complex **2** gave the desired hydroborated product in 95% yield along with 5% *p*-methoxyethylbenzene (eq 2). Catalytic reaction mixtures containing excess borane even suppressed formation of the small amounts of vinylboronate ester and alkylarene product obtained in the absence of the excess borane (eq 3).



Mechanistic studies were conducted on the titanium-catalyzed reaction between *p*-methoxystyrene and excess  $\text{HBcat}'$  involving bis(borane) **2**. All studies were performed at temperatures below  $-5$  °C. Initially, we sought to identify potential reaction intermediates and the catalyst resting state. A toluene- $d_8$  solution of *p*-methoxystyrene and  $\text{HBcat}'$  was added to complex **2** at  $-78$  °C. When the temperature was raised to  $-20$  °C (at which point the catalytic reaction occurred),  $^1\text{H}$  NMR spectroscopy showed complex **2** to decay slowly. No new titanium species were observed by NMR spectroscopy.

To investigate whether **2** was converted to a catalytically active paramagnetic species, we probed the early stages of reaction for an induction period. No induction period was observed, and the disappearance of **2** occurred on the same time scale as the catalytic reaction. The latter result rules out the possibility that the induction period is too rapid to detect. To provide further

**Table 2. Initial Rates of Alkene Hydroboration Catalyzed by **1** at Varying Concentrations of *p*-Methoxystyrene and  $\text{HBcat}'$ <sup>a</sup>**

[ <i>p</i> -methoxystyrene], M	[ $\text{HBcat}'$ ], M	initial rate, $10^6 \text{ M s}^{-1}$
0.0695	0.209	-8.01
0.0695	0.348	-4.52
0.0695	0.695	-2.96
0.0695	1.04	-2.13
0.0695	1.39	-1.36
0.0174	0.348	-1.18
0.0348	0.348	-2.67
0.104	0.348	-6.44
0.139	0.348	-11.5

Rates were measured by  $^1\text{H}$  NMR spectroscopy at  $-20$  °C over the first 1000 s of reaction.

evidence that **2** is converted to a catalytically inactive species, two  $\text{Ti}(\text{III})$  complexes,  $\text{Cp}_2\text{Ti}(\text{H}_2\text{Bcat}')(\text{3})$  and fulvalene complex  $[(\text{C}_{10}\text{H}_8)\text{Cp}_2\text{Ti}_2\text{H}_2](\text{4})$ ,<sup>42</sup> which are known to be decomposition products of the titanocene bis(borane) complexes,<sup>31</sup> were tested for catalytic activity. Borohydride **3** promoted alkene hydroboration, but at a rate that was slower than reactions catalyzed by **2** (32% yield for **3** vs 95% yield for **2** after 1 h at  $-5$  °C). Fulvalene **4** showed no activity as a hydroboration catalyst. Thus, complex **2** is most likely responsible for the catalytic chemistry.

Kinetic studies were conducted to determine how **2** catalyzes the reaction. Catalyst decomposition occurred in competition with the hydroboration chemistry; therefore, the method of initial rates was most appropriate for our kinetic studies.<sup>43</sup> The *p*-methoxystyrene concentration was monitored by  $^1\text{H}$  NMR spectroscopy over the first 1000 s of reaction at  $-20$  °C. Over this time period, the catalyst concentration decreased by less than 5%, and good linear fits for the decay of alkene over this time period were obtained. Excess  $\text{HBcat}'$  was used in all experiments to prevent competing hydrogenation. The values of the initial rates at different alkene and  $\text{HBcat}'$  concentrations are presented in Table 2.

The order of the reaction in alkene concentration was determined for reactions with concentrations of *p*-methoxystyrene between 0.0695 and 0.139 M. The concentrations of  $\text{HBcat}'$  and catalyst were constant at 0.348 M and 6.95 mM, and rate measurements were made by monitoring the disappearance of alkene. The  $\ln[\text{alkene}]$  vs  $\ln(\text{initial rate})$  plot provided a slope of 1.0, demonstrating a first-order rate dependence on alkene concentration. The order of the reaction in  $\text{HBcat}'$  concentration was determined by obtaining initial rates for reactions with concentrations of  $\text{HBcat}'$  between 0.209 and 1.39 M. Rate measurements were made by monitoring the disappearance of alkene. In each run, the initial alkene and catalyst concentrations were 69.5 and 6.95 mM. The  $\ln[\text{HBcat}']$  vs  $\ln(\text{initial rate})$  plot provided a slope of  $-0.87$ , indicating a rate dependence that is near inverse first order. This inverse order in borane concentration is unusual for a reactant in a catalytic process.

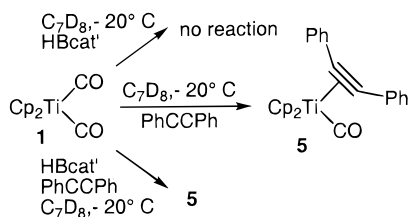
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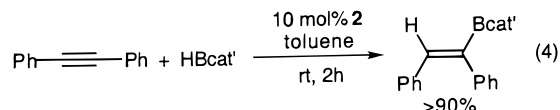
(43) For a review of initial rate method see: Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes*; VCH: Weinheim, Germany, 1991; p 465.



## Scheme 1

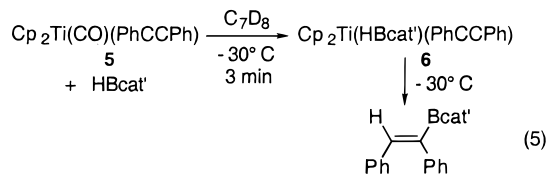


were conducted on reactions of alkynes and borane reagents with **1** at  $-20^{\circ}\text{C}$  to identify which species reacted with **1** to initiate the catalytic reaction in eq 4

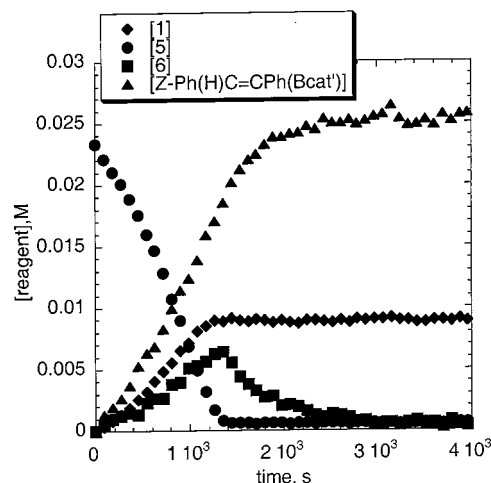


and Scheme 1. Addition of a toluene- $d_8$  solution of PhCCPh to **1** resulted in the formation of  $\text{Cp}_2\text{Ti}(\text{CO})(\text{PhCCPh})$  (**5**) after 2.5 h at  $-20^{\circ}\text{C}$ . Similar reactions have been conducted at room temperature.<sup>44</sup> Most important for the catalytic studies, the reaction of equimolar quantities of HBcat', PhCCPh, and **1** produced alkyne carbonyl complex **5** in addition to unreacted **1**. The concentration of **5** steadily increased over 24 h at  $-30^{\circ}\text{C}$  but never exceeded that of **1**. The hydroboration product  $\text{Ph}(\text{H})\text{C}=\text{C}(\text{Ph})(\text{Bcat}')$  was generated slowly over this time period, but only after the appearance of compound **5**. These observations suggested that the formation of **5** from reaction of **1** with PhCCPh initiates hydroboration of PhCCPh.

The alkyne carbonyl complex **5** was reacted with HBcat' for the purpose of observing the formation of intermediates en route to B–C bond formation. At room temperature, this reaction rapidly gave vinylboronate ester. However, addition of 1 equiv of HBcat' to a toluene- $d_8$  solution of complex **5** at  $-30^{\circ}\text{C}$  resulted in the formation of  $\text{Cp}_2\text{Ti}(\text{HBcat}')(\text{PhCCPh})$  (**6**) after 3 min, as determined by  $^1\text{H}$  NMR spectroscopy (eq 5). It is important to note that the vinylboronate ester product was generated slowly, after the initial appearance of compound **6**.

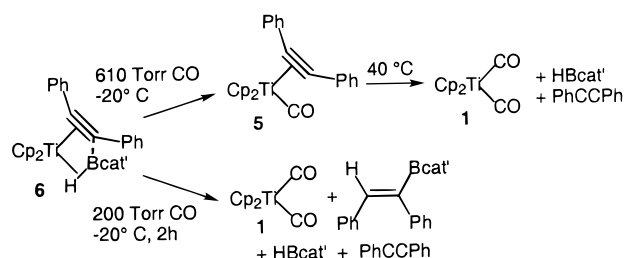


The reaction between **5** and HBcat' was conducted with 3 equiv of HBcat' to ensure that the  $\text{Cp}_2\text{Ti}$  fragment would be trapped by excess borane. Dicarboxyl complex **1** and bis(borane) complex **2** were formed after warming to  $-20^{\circ}\text{C}$ . The formation of the products as a function of time is shown in Figure 1. The convex trace for the decay of **5** and the concave trace for the appearance of vinylboronate ester suggest autocatalytic behavior. In this case, one of the products of the reaction should react with **5**. Indeed, bis(borane) **2** reacted with

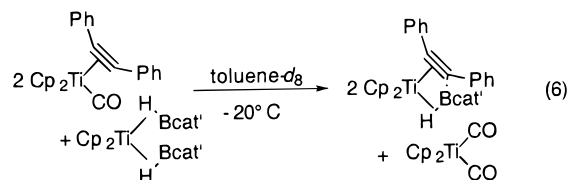


**Figure 1.** Concentrations of  $\text{Cp}_2\text{Ti}(\text{CO})_2$  (**1**),  $\text{Cp}_2\text{Ti}(\text{CO})(\text{PhCCPh})$  (**5**),  $\text{Cp}_2\text{Ti}(\text{HBcat}')(\text{PhCCPh})$  (**6**), and vinylboronate ester for the reaction of **5** and HBcat' at  $-20^{\circ}\text{C}$ .

## Scheme 2



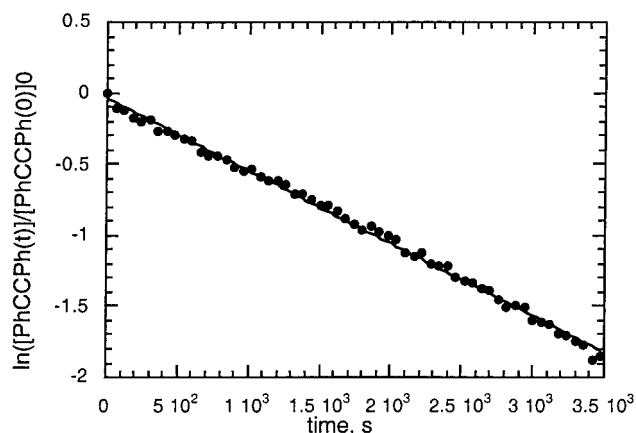
**5** to give alkyne borane complex **6** and titanocene dicarbonyl rapidly at  $-30^{\circ}\text{C}$  (eq 6). Previously we have



shown that bis(borane) **2** and dicarbonyl **1** are favored thermodynamically over  $\text{Cp}_2\text{Ti}(\text{CO})(\text{HBcat}')$ . Thus, the kinetic behavior of catalytic systems involving alkyne complexes as resting states would be complex.

The reversibility of the formation of intermediate complexes **5** and **6** was assessed. The first step is known to be reversible, since  $\text{Cp}_2\text{Ti}(\text{CO})(\text{PhCCPh})$  reacts with CO to form  $\text{Cp}_2\text{Ti}(\text{CO})_2$ .<sup>44</sup> The reversibility of the formation of complex **6** was determined by reacting it with CO and monitoring the reaction by low-temperature  $^1\text{H}$  NMR spectroscopy. As shown in Scheme 2, addition of 610 Torr of CO pressure to complex **6** at  $-78^{\circ}\text{C}$  resulted in displacement of HBcat' and formation of alkyne carbonyl **5**. No vinylboronate ester was generated. After the temperature was increased from  $-80$  to  $40^{\circ}\text{C}$ , dicarbonyl **1**, free alkyne, and free borane were formed. An identical experiment that used a lower pressure of CO (200 Torr) led to formation of free alkyne and free borane in competition with vinylboronate ester and titanocene dicarbonyl. Thus, the formation of vinylboronate ester from complex **6** competes with regeneration of **1**, and the relative rates depend on the pressure of CO.

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**Figure 2.** Natural logarithm of the decay of PhCCPh as a function of time ([PhCCPh] = 0.0625 M, [HBcat] = 0.310 M, [1] = 6.25 mM,  $P_{\text{CO}}$  = 122 Torr).

**Table 3. Values of  $k_{\text{obs}}$  at Varying Concentrations of HBcat'**<sup>a</sup>

[HBcat'], M	$k_{\text{obs}}$ , $10^4 \text{ s}^{-1}$	[HBcat'], M	$k_{\text{obs}}$ , $10^4 \text{ s}^{-1}$
0.313	$1.4 \pm 0.3$	0.938	1.8
0.625	$2.2 \pm 0.1$	1.25	2.1

<sup>a</sup> Conditions: [tolCCtol] = 0.0625 M, [1] = 6.25 mM,  $P_{\text{CO}}$  = 200 Torr.

Because observed species often do not lie on the catalytic cycle, we conducted kinetic studies to investigate whether the rate law was consistent with the intermediacy of complexes **5** and **6**. The experiments were performed using either PhCCPh or *p*-tolCC-*p*-tol as alkyne and HBcat, HBcat-4-*t*-Bu (HBcat'), or HBcat-4-Me as borane. The dependence of reaction rate on the concentration of alkyne was obtained by monitoring the disappearance of PhCCPh or *p*-tolCC-*p*-tol in the presence of excess of the borane and added CO. The reaction rate was measured at 40 °C with a 0.0625 M initial concentration of PhCCPh, a concentration of HBcat' of 0.313 M, and a concentration of  $\text{Cp}_2\text{Ti}(\text{CO})_2$  of 6.25 mM. To create a single resting state and to avoid compound **5** with its accompanying complex autocatalytic chemistry (vide supra) as resting state, we conducted reactions under 122 Torr of carbon monoxide to ensure that the resting state was **1**. The reaction rate showed a first-order dependence on the concentration of PhCCPh, as shown in Figure 2.

The dependence of the rate of reaction on borane concentration was determined by two methods. The first involved obtaining values of  $k_{\text{obs}}$  in the presence of 200 Torr of added CO at various concentrations of excess borane. The  $k_{\text{obs}}$  values in Table 3 show that the reaction became zero order in borane as borane concentration was increased. Because the dependence of borane at low concentrations was ambiguous, a second method was used to evaluate the reaction order at these low concentrations. This method involved monitoring the decay of a 0.0625 M solution of HBcat' in the presence of excess (0.375 M) of PhCCPh, 700 Torr of added CO, and 10 mol % of catalyst at 40 °C. A large CO pressure was required to prevent the accumulation of  $\text{Cp}_2\text{Ti}(\text{CO})_2$  (PhCCPh) (**2**) in solution at this high alkyne concentration. Under these reaction conditions, the decay of borane was first order.

**Table 4. Values of  $k_{\text{obs}}$  at Varying CO Pressures<sup>a</sup>**

$P_{\text{CO}}$ , Torr	$k_{\text{obs}}$ , $10^5 \text{ s}^{-1}$	$P_{\text{CO}}$ , Torr	$k_{\text{obs}}$ , $10^5 \text{ s}^{-1}$
100	130	200	29.0
110	113	300	12.5
132	64.8	600	4.23

<sup>a</sup> Conditions: [PhCCPh] = 0.0625 M, [HBcat'] = 0.313 M, [1] = 0.00625 M.

**Table 5. Product Ratios for Hydroboration of 1-Hexyne with Different Catalysts (4 mol %)**

$\text{Cp}_2\text{TiMe}_2$	76	2	11	11
$\text{Cp}_2\text{Ti}(\text{HBcat})_2$	75	2	16	8
$\text{Cp}_2\text{Ti}(\text{CO})_2$	96	0	2	2

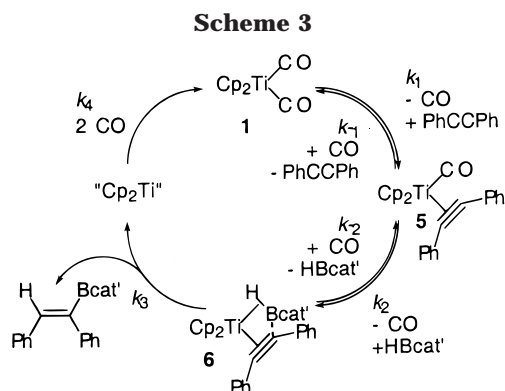
The reaction order in added CO was evaluated from observed rate constants for the decay of alkyne (0.0625 M initial concentration) in the presence of 1.25 M HBcat' and 6.25 mM **1** at 40 °C. The values of  $k_{\text{obs}}$  were obtained for CO pressures ranging from 63 Torr to 400 Torr. A plot of  $\ln(k_{\text{obs}})$  vs  $\ln(P_{\text{CO}})$  provided a rate dependence that was less than inverse second order (−1.7). The dependence of rate on CO pressure was also determined by monitoring the disappearance of PhCCPh in the presence of a lower 0.313 M concentration of borane at CO pressures ranging from 100 to 600 Torr. The values of  $k_{\text{obs}}$  at different CO pressures are presented in Table 4. In this case, the rate dependence on the pressure of added CO was within experimental error of inverse second order (−1.9).

To determine if different titanocene hydroboration catalysts generate the same reactive intermediates, the selectivities of several catalysts were compared. A solution of 1-hexyne and HBcat' in ether was added to catalytic quantities of titanocene dimethyl, bis(borane) complex **1**, and dicarbonyl **2** at room temperature. Table 5 shows that  $\text{Cp}_2\text{TiMe}_2$  and  $\text{Cp}_2\text{Ti}(\text{HBcat})_2$  yielded similar mixtures of products. The major hydroboration product was the anti-Markovnikov vinylboronate ester, but the Markovnikov product was also formed in small quantities. In addition, both systems yielded products of hydrogenation. In agreement with earlier experiments, titanocene dicarbonyl gave exclusively anti-Markovnikov hydroboration products, with only trace amounts of hydrogenation products detected.

## Discussion

Our mechanistic studies were directed at identifying intermediates in the catalytic cycles of alkene and alkyne hydroboration and determining the sequence of ligand dissociation and association involved in the formation of these intermediates. We were interested in determining whether borane complexes that we had previously isolated and characterized were intermediates in the hydroboration and, in particular, how the bis(borane) complexes catalyzed the hydroboration of alkenes.

Our studies on stoichiometric reactions of the catalytic cycle for alkyne hydroboration catalyzed by dicarbonyl complex **1** suggested the pathway shown in Scheme 3 that involves alkyne carbonyl **5** and alkyne borane complex **6** on the catalytic cycle. In addition, our stoichiometric studies showed that the formation of the



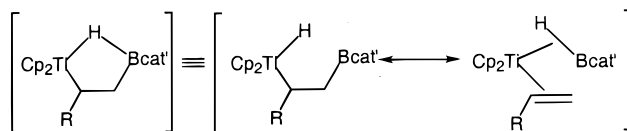
alkyne borane complex **6** is highly reversible when 600 Torr of CO is present and partially reversible when 200 Torr of CO is present. Because the formation of **5** and **6** is reversible in the presence of CO,<sup>44</sup> it was likely that these complexes could regenerate dicarbonyl **1**, which could then catalyze the reaction through a different set of intermediates. Kinetic studies were, therefore, conducted to determine whether **5** and **6** are true intermediates.

Equation 7 is a rate expression for the pathway in Scheme 3 that assumes the two preequilibria  $K_1$  and  $K_2$ . According to this expression, the rate of the reaction

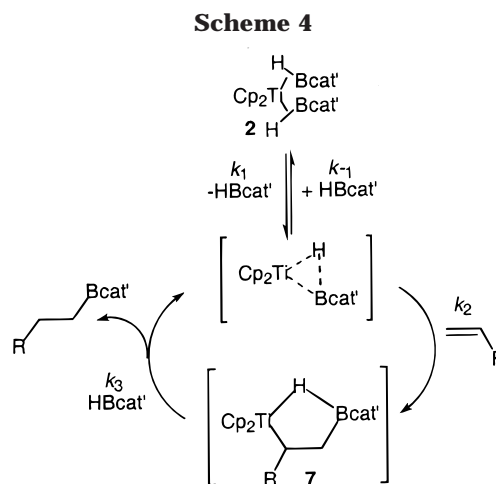
$$\text{rate} = \frac{k_3 K_1 K_2 [\mathbf{1}] [\text{PhCCPh}] [\text{HBcat}']}{[\text{CO}]^2} \quad (7)$$

would be first order in the concentration of PhCCPh and HBcat' and inverse second order in added CO. Our kinetic experiments at 0.0625 M or less of borane showed a first-order dependence on the concentration of alkyne and borane and an inverse second-order dependence on added CO. Thus, our kinetic results are consistent with the proposed mechanism.

However, the dependence of the reaction rate on borane concentration appeared to vary with the concentration of borane. The values of  $k_{\text{obs}}$  given in Table 3 suggest that the reaction rate has a positive dependence on the concentration of HBcat' at borane concentrations below 0.0625 M (10 equiv vs alkyne), and this behavior is confirmed by separate experiments in which the decay of borane concentration is monitored and is shown to be first order. However, the reaction rate began to show no dependence on borane concentration above this concentration. Thus, the value of  $k_2[\text{HBcat}']$  appears to approach that of  $k_{-1}[\text{CO}]$  in Scheme 3 when  $[\text{HBcat}']$  is higher. This relative rate would cause the second step in the proposed mechanism to become only partially reversible. The rate expression would then show an order in borane that is less than 1 and a dependence on added CO that is between inverse first and inverse second order. Our data suggest that we have established this kinetic situation. The order in borane under these conditions is certainly less than 1, and the plot of  $\ln(P_{\text{CO}})$  vs  $\ln(k_{\text{obs}})$  provided a slope of  $-1.7$ , indicating an order in CO that is between inverse first and inverse second. Considering the absence of added CO under standard synthetic conditions that would employ catalyst **1**, the reaction of **6** to give product would be faster than reversion to **5** or **1** in this case. Moreover, alkyne carbonyl **5** accumulates under condi-



**Figure 3.** Proposed structure of the alkene borane intermediate.



tions of low  $P_{\text{CO}}$  and high concentrations of alkyne, making the resting state a combination of both **1** and **5** under these conditions.

**Mechanistic Studies of the Alkene Hydroboration Catalyzed by 2.** Mechanistic studies were performed to determine whether complexes related to **6** were responsible for the hydroboration of alkenes catalyzed by bis(borane) complex **2**. Previous reports contradicted our observation of clean hydroboration of alkenes catalyzed by  $\text{Cp}_2\text{TiMe}_2$  via complex **2**;<sup>30</sup> thus, our study was also directed at confirming that complex **2** behaved as a true hydroboration catalyst. A mechanism that involves **2** and that fits the experimental data presented below is shown in Scheme 4.

Our studies showed that the titanocene bis(borane) complex decayed during catalytic hydroboration but that this decay was like any common catalyst decomposition. It did not generate a second species that was the true catalyst. The absence of an induction period, coupled with the direct observation of catalyst decay on the time scale of product formation, demonstrates that **2** was responsible for the catalytic chemistry. Further, two paramagnetic Ti(III) species that are known decomposition products of **2**, borohydride **3** and fulvalene **4**, catalyzed hydroboration more slowly than did complex **2**.

The mechanism in Scheme 4 involves initial dissociation of coordinated borane to generate a monoborane intermediate. Coordination of alkene would generate the alkene borane complex **7**, which is similar to a species isolated by Erker.<sup>45</sup> A  $\beta$ -borylalkyl hydride structure with  $\text{B}\cdots\text{H}$  stabilization (Figure 3) is certainly an important resonance structure of **7**. An intramolecular reaction would extrude the alkylboronate ester product, and coordination of HBcat' would regenerate the monoborane intermediate. The rate law for the proposed mechanism derived by a steady-state approximation for

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the monoborane intermediate and irreversible formation of the alkene borane complex is shown in eq 8. Excess borane was used in our experiments, and under these conditions the rate law may simplify to eq 9. Our

$$\text{rate} = \frac{k_1 k_2 [1][\text{alkene}]}{k_{-1} [\text{HBcat}'] + k_2 [\text{alkene}]} \quad (8)$$

$$\text{rate} = \frac{k_{\text{obs}} [1][\text{alkene}]}{[\text{HBcat}']} \quad (9)$$

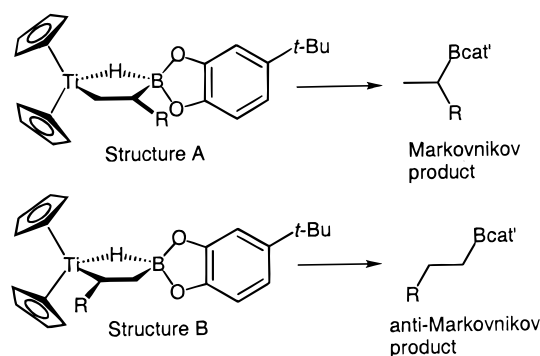
mechanistic studies provided a first-order rate dependence on the concentration of alkene and an inverse first-order rate dependence on the concentration of borane. These data agree with the proposed mechanism in Scheme 4.

The inverse order in borane was unexpected because borane is a reagent for the catalytic process. However, the isolation of **2** showed that borane was not only a reagent but also a ligand on the resting state of the catalyst. Borane behaves in this process like carbon monoxide in catalytic carbonylations. In many carbonylation processes, carbon monoxide acts as a ligand and as a reagent. Thus, some reaction conditions and catalysts provide a first-order dependence on CO concentration, while others show an inverse dependence of rate on CO.<sup>46</sup> Of course, this inverse dependence arises because reversible CO dissociation creates a site for alkene coordination. The same kinetic behavior occurs with **2**, except it is dissociation of the uncommon ligand catecholborane that allows for alkene coordination.

**Pathways for Catalyst Decomposition.** A requirement for a true catalyst is that decomposition occurs by a pathway separate from the catalytic cycle. One possibility for catalyst decomposition is  $\beta$ -hydrogen elimination rather than reductive elimination from the alkene borane intermediate to generate titanium hydrides. The dihydride product from  $\beta$ -hydrogen elimination may react with alkene to give alkylarene, thereby regenerating  $\text{Cp}_2\text{Ti}$  and ultimately **2**. Titanocene hydride complexes are also known to undergo dimerization to form stable compounds.<sup>47</sup> A second path for catalyst decomposition is conversion of the titanocene intermediate to inactive complexes by reaction chemistry that competes with coordination of borane to re-form **2**.

We offer two possible beneficial effects of excess borane. First, the reductive elimination step may be induced by free borane, thereby making this step favored over  $\beta$ -hydrogen elimination at high borane concentrations. However, we previously studied the extrusion of vinylboronate ester from alkyne borane complex **6** and showed that this reaction was zero order in added borane.<sup>48</sup> Thus, borane-induced reductive elimination from alkene borane complex **7** is unlikely. Instead, efficient trapping of the titanocene by borane to regenerate the catalyst resting state **2** may account for the higher yields in the presence of free borane. We favor this proposal, but one must also rationalize the

Scheme 5



lower yields for formation of alkylboronate ester from stoichiometric reactions of isolated **2** with styrenes in the absence of borane. Perhaps the initial metal product titanocene reacts with **2** in this case to form a complex set of reactive intermediates and Ti(III) complexes. Under these conditions, a high concentration of catecholborane would lead to efficient trapping of titanocene and prohibit its interference in the reactions of **2** with alkenes.

**Origin of Regioselectivity.** Anti-Markovnikov products were the major isomers formed by this catalytic hydroboration. Possible geometries of the alkene borane intermediate are shown in Scheme 5. The R group of structure A is positioned away from the Cp rings but adjacent to the catechol substituent. The perpendicular alignment of the catechol may cause steric interactions between the R group and the catecholborane that are more severe than the interactions of R with the Cp ligands. Perhaps more important, the electron-rich metal-bound carbon in structure B is stabilized by the electron-withdrawing aryl group. The reduced regioselectivity with alkenes reported previously<sup>31</sup> may reflect the decreased electronic preference for structure B.

**Conclusion.** Our mechanistic studies have revealed the intermediacy of several borane complexes in catalytic hydroboration processes involving titanocene. First, bis(borane) complex **2** appears to be the active catalyst for the hydroboration of alkenes originally catalyzed by titanocene dimethyl. This catalyst dissociates borane to generate a monoborane intermediate. This intermediate coordinates alkene to give a complex that is likely to be a resonance hybrid between an alkene borane complex and a  $\beta$ -borylalkyl hydride. The hydroboration of alkynes involves a similar complex that we have characterized previously and that is best described as a resonance hybrid between an alkyne borane complex and a  $\beta$ -borylvinyl hydride. The greater stability of the dicarbonyl catalyst for alkyne hydroboration compared to that of the bis(borane) catalyst for alkene hydroboration may result from a more efficient trapping of titanocene by CO rather than by the unusual and weakly bound ligand catecholborane. The dual purpose of catecholborane as substrate and ligand provides the inverse reaction order in borane, as is often seen in carbonylation chemistry when CO acts as a substrate and ligand.

## Experimental Section

**General Considerations.** Unless otherwise noted, all manipulations were conducted using standard Schlenk tech-

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niques or an inert-atmosphere glovebox.  $^1\text{H}$  NMR spectra were obtained on a GE QE 300 MHz, GE  $\Omega$  300 MHz, or a GE  $\Omega$  500 MHz Fourier transform spectrometer and were recorded relative to residual protiated solvent.  $^{11}\text{B}$  NMR spectra were obtained on the GE QE 300 MHz spectrometer operating at 96.38 MHz.  $^{11}\text{B}$  NMR chemical shifts are reported in units of parts per million downfield from  $\text{BF}_3\cdot\text{OEt}_2$  as an external standard. GC measurements were made on a Hewlett-Packard 5890 Series II gas chromatograph.

Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification.  $\text{Cp}_2\text{Ti}(\text{PhCCPh})(\text{CO})$  (**5**),<sup>44</sup>  $\text{Cp}_2\text{Ti}(\text{PhCCPh})$ ,<sup>49</sup>  $\text{tolCCtol}$ ,<sup>50</sup> 4-*tert*-butylcatecholborane (HBcat'),<sup>48</sup>  $\text{Cp}_2\text{Ti}(\text{HBcat}')_2$  (**2**),<sup>48</sup>  $\text{Cp}_2\text{Ti}(\text{HBcat}')_2$ ,<sup>48</sup>  $\text{Cp}_2\text{Ti}(\text{H}_2\text{Bcat}')_2$  (**3**),<sup>31</sup>  $[(\text{C}_{10}\text{H}_8)\text{Cp}_2\text{Ti}_2\text{H}_2]$  (**4**),<sup>42</sup> and  $\text{Cp}_2\text{TiMe}_2$ <sup>51</sup> were prepared by published procedures. All protiated solvents were dried over purple sodium benzophenone ketyl and were obtained by distillation under nitrogen. The deuterated solvents were dried as their protiated analogues, but were obtained by vacuum distillation from the drying agent.

#### Reactions of Alkenes with HBcat' Catalyzed by **2**–**4**.

An NMR tube was charged with **2** (2.2 mg, 0.0042 mmol), and the tube was sealed with a septum. A separate vial was charged with alkene (0.042 mmol), HBcat' (7.3 mg, 0.042 mmol), and ferrocene internal standard in  $\text{C}_7\text{D}_8$  (0.6 mL). An initial NMR spectrum was obtained on this sample. This solution was then added to the catalyst at room temperature or at  $-78^\circ\text{C}$  for reactions employing catalysts **2**–**4** at  $-5^\circ\text{C}$ . The sample was shaken to dissolve all the solid and kept at room temperature for 10 min and at  $-5^\circ\text{C}$  for 5 h, at which time it was analyzed by  $^1\text{H}$  NMR spectrometry. 4-MeOC<sub>4</sub>H<sub>4</sub>-CH<sub>2</sub>CH<sub>2</sub>BO<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-4-*t*-Bu:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.16 (s, 9H), 1.47 (t,  $J$  = 8.0 Hz, 2H), 2.85 (d,  $J$  = 8.0 Hz, 2H), 3.28 (s, 3H), 6.75 (d,  $J$  = 8.6 Hz, 2H), 6.89 (dd,  $J$  = 8.4, 1.8 Hz, 1H), 7.03 (m, 3H), 7.25 (d,  $J$  = 1.6 Hz, 1H);  $^{11}\text{B}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  35 (s). 2-Ethylindenyl-Bcat':  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.17 (s, 9H), 2.10 (pentet,  $J$  = 9.1 Hz, 1H), 3.05 (dd,  $J$  = 15.5, 9.1 Hz, 2H), 3.17 (dd,  $J$  = 15.5, 9.1 Hz, 2H), 6.88 (dd,  $J$  = 8.3, 1.4 Hz, 1H), 6.98 (d,  $J$  = 8.3 Hz, 1H), 7.05–7.12 (m, 4H), 7.20 (d,  $J$  = 1.4 Hz, 1H);  $^{11}\text{B}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  35.7 (s).

**Reaction of Alkynes with HBcat' Catalyzed by **1**.** A vial was charged with alkyne (0.0379 or 0.0910 mmol), either HBcat' (6.6 mg, 0.0375 mmol) or catecholborane (109 mg, 0.910 mmol), ferrocene internal standard, and **1** (2.0 mg, 0.0085 mmol or 8.5 mg, 0.036 mmol). The NMR tube was left at room temperature for 2–3 h. The solution was then analyzed by  $^1\text{H}$  NMR spectroscopy or gas chromatography. Identical procedures were used for the reaction of 1-hexyne and HBcat catalyzed by titanocene dimethyl. *p*-tolCHC(Bcat')-*p*-tol:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.18 (s, 9H), 1.94 (s, 3H), 2.14 (s, 3H), 6.75 (d,  $J$  = 8.0 Hz, 2H), 6.89 (dd,  $J$  = 8.3 Hz, 1.9 Hz, 1H), 7.02 (d,  $J$  = 8.4 Hz, 1H), 7.07 (d,  $J$  = 7.8 Hz, 2H), 7.20 (m, 3H), 7.32 (d,  $J$  = 7.8 Hz, 2H), 7.99 (s, 1H);  $^{11}\text{B}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  32; HRMS (EI) calcd 382.2104, found 382.2099. PhCHC(Bcat')Ph:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.18 (s, 9H), 6.8–7.22 (m, 11H), 7.32 (d,  $J$  = 7.3 Hz, 2H), 7.95 (s, 1H);  $^{11}\text{B}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  32.

**Reaction of **2** with *p*-Methoxystyrene.** An NMR tube was charged with **2** (5.0 mg, 0.0095 mmol), and the tube was sealed with a septum. The tube was cooled to  $-78^\circ\text{C}$ , and a solution of methoxystyrene (3.8  $\mu\text{L}$ , 0.029 mmol) in  $\text{C}_7\text{D}_8$  (0.6 mL) was added by syringe. The sample was shaken to dissolve all the solid without allowing it to warm. The sample was maintained at  $-30^\circ\text{C}$  for 4 h and then quickly immersed into the precooled probe ( $-30^\circ\text{C}$ ) of the NMR spectrometer for analysis.

**Reaction of *p*-Methoxystyrene, HBcat', and Stoichiometric Amounts of **2**.** A solution of *p*-methoxystyrene (1.3  $\mu\text{L}$ , 0.0095 mmol) and HBcat' (1.7 mg, 0.0095 mmol) in  $\text{C}_6\text{D}_6$  (0.6 mL) was added to a vial containing **2** (5.0 mg, 0.0095 mmol). The resulting solution was analyzed by  $^1\text{H}$  NMR spectroscopy after 10 min.

**Reaction of Diphenylacetylene, HBcat', and Stoichiometric Amounts of **1**.** A vial was charged with PhCCPh (4.50 mg, 0.0250 mmol), and the solid was dissolved in 0.2 mL of toluene- $d_8$ . The solution was transferred to an NMR tube, and the tube was sealed with a septum. The tube was then cooled to  $-78^\circ\text{C}$  and was charged with a toluene- $d_8$  solution (0.4 mL) of HBcat' (4.40 mg, 0.0250 mmol) and **1** (5.9 mg, 0.0250 mmol) by syringe. The NMR tube was shaken without allowing it to warm and was quickly inserted into the precooled probe ( $-30^\circ\text{C}$ ) of the NMR spectrometer for analysis.

**Reaction of **1** with HBcat'.** A vial was charged with **1** (10 mg, 0.0427 mmol), and the solid was dissolved in 0.6 mL of toluene- $d_8$ . HBcat' was added (37.6 mL, 0.214 mmol), and the mixture was transferred to an NMR tube. The sample was cooled to  $-10^\circ\text{C}$  and analyzed by  $^1\text{H}$  NMR spectroscopy after 30 min.

**Reaction of **5** with HBcat'.** A vial was charged with alkyne carbonyl **5** (5.6 mg, 0.0140 mmol), and the solid was dissolved in 0.6 mL of toluene- $d_8$ . The solution was transferred to an NMR tube, and the tube was sealed with a septum. The tube was then cooled to  $-78^\circ\text{C}$ , and HBcat' (2.5  $\mu\text{L}$ , 0.0140 mmol) was added to the NMR tube by syringe. The NMR tube was shaken without allowing it to warm and was quickly inserted into the precooled probe ( $-30^\circ\text{C}$ ) of the NMR spectrometer for analysis.

**Reaction of **2** with **5**.** An NMR tube was charged with **2** (2.3 mg, 0.0057 mmol) and **5** (3.0 mg, 0.0057 mmol), and the tube was sealed with a septum. The tube was then cooled to  $-78^\circ\text{C}$ , and 0.6 mL toluene- $d_8$  was added by syringe. The NMR tube was shaken without allowing it to warm and was quickly inserted into the precooled probe ( $-20^\circ\text{C}$ ) of the NMR spectrometer for analysis.

**Reaction of **6** with CO.** A vial was charged with  $\text{Cp}_2\text{Ti}(\text{PhCCPh})$  (2.4 mg, 0.00674 mmol), and the solid was dissolved in toluene- $d_8$  (0.6 mL). The solution was transferred by syringe into a medium-walled Young NMR tube. HBcat' was added to the tube (1.2  $\mu\text{L}$ , 0.0067 mmol) by syringe onto the wall of the NMR tube, with care taken to prevent mixing with the solution. The tube was closed and quickly cooled to  $-190^\circ\text{C}$ . The tube was evacuated at this temperature and was then charged with 610 Torr of CO at  $-78^\circ\text{C}$ . The tube was sealed, shaken without allowing it to warm, and quickly inserted into the precooled probe ( $-30^\circ\text{C}$ ) of the NMR spectrometer for analysis. The experiment was repeated using 133 Torr of CO added at  $-78^\circ\text{C}$ .

**Kinetic Studies on the Addition of Catecholboranes to Alkynes Catalyzed by **1**.** Studies were performed using neat HBcat' and stock solutions of *p*-tolCC-*p*-tol (0.3636 M) and  $\text{Cp}_2\text{Ti}(\text{CO})_2$  (0.214 M) in  $\text{C}_6\text{D}_6$ . Reaction rates were measured by  $^1\text{H}$  NMR spectroscopy in the spectrometer probe using single-pulse experiments performed every 90 s, using an automated program for at least 3 half-lives. A vial was charged with HBcat (20.0  $\mu\text{L}$ , 0.188 mmol) and aliquots of the stock solutions of  $\text{tolCCtol}$  (103  $\mu\text{L}$ , 0.0375 mmol) and  $\text{Cp}_2\text{Ti}(\text{CO})_2$  (**1**; 17.6  $\mu\text{L}$ , 0.00375 mmol). Benzene- $d_6$  (0.46 mL) was added to the vial, and the mixture was transferred by pipet into an NMR tube. The solution was degassed, the tube was charged with 200 Torr of CO pressure at room temperature, and the tube was flame-sealed. The NMR tube was shaken and inserted into the probe of the NMR spectrometer for analysis. Rate measurements were performed at  $40^\circ\text{C}$  by measuring the integral of the *p*-tolyl resonance of the alkyne.

The experiment was repeated using 110, 132, 200, 300, and 600 Torr of CO pressure to determine the order in CO. To determine the order in borane, the experiment was repeated

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using 40.0, 60.0, and 80.0  $\mu\text{L}$  of added HBcat. Alternatively, a vial was charged with PhCCPh (40.0 mg, 0.225 mmol),  $\text{HBO}_2\text{C}_6\text{H}_3\text{-4-Me}$  (5.01 mg, 0.0375 mmol), and  $\text{Cp}_2\text{Ti}(\text{CO})_2$  (**1**; 17.6  $\mu\text{L}$ , 0.00375 mmol). Benzene- $d_6$  (0.6 mL) was added to the vial, and the mixture was transferred by pipet into an NMR tube. The solution was degassed, and the tube was charged with 436 Torr of CO pressure at  $-78^\circ\text{C}$  and flame-sealed. The NMR tube was shaken and inserted into the probe of the NMR spectrometer for analysis. Rate measurements were performed by measuring the integrals of the methyl resonance of the borane. The NMR tube was shaken and inserted into the probe of the NMR spectrometer for analysis at  $40^\circ\text{C}$ . Rate measurements were performed by measuring the integral of the *p*-tolyl peak of the alkyne.

**Profile of the Reaction between 5 and 3 Equiv of HBcat'.** A vial was charged with **5** (5.6 mg, 0.014 mmol), and the solid was dissolved in toluene- $d_8$  (0.6 mL). The solution was transferred into an NMR tube, and the tube was sealed with a septum. The tube was then cooled to  $-78^\circ\text{C}$ , and HBcat' (7.5  $\mu\text{L}$ , 0.042 mmol) was added to the NMR tube by syringe. The NMR tube was shaken without allowing it to warm and was quickly inserted into the precooled probe ( $-20^\circ\text{C}$ ) of the NMR spectrometer for analysis. Single-pulse experiments were performed every 60 s using an automated program. Concentrations were determined from the integrals of the Cp peaks of **1**, **2**, and **5**, as well as the vinyl peak of (Ph)(H)C=C(Bcat')-(Ph).

**$\text{Cp}_2\text{Ti}(\text{catBCH}=\text{CHPh})$ .** A vial containing  $\text{Cp}_2\text{Ti}(\text{HBcat})_2$  (800 mg, 1.91 mmol) was charged with a solution of phenylacetylene (390 mg, 3.82 mmol) in 15 mL of toluene, and the mixture was stirred at room temperature. After 2 h, the solvent was evaporated under vacuum, leaving a dark brown paste. This material was rinsed with small quantities of pentane to remove unreacted alkyne. The residual dark brown solid was dissolved in ether, and the resulting solution was stored at  $-30^\circ\text{C}$  for 3 days. The dark red-brown product precipitated, and the supernatant was removed by pipet. Analytically pure red-brown solid (101 mg, 13% yield) was obtained by recrystallization from ether.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.11 (m, 5H), 6.86 (m, 4H), 6.35 (s, 5H), 6.03 (s, 5H), 5.65 (d,  $J = 14.5$  Hz, 1H), 4.16 (d,  $J = 14.0$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  150.87, 148.87,

127.56, 127.26, 123.08, 123.00, 121.85, 119.05 (Cp), 117.93 (Cp), 111.54.  $^{11}\text{B}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  33.4. Anal. Calcd for  $\text{C}_{24}\text{H}_{21}\text{-BO}_2\text{Ti}$ : C, 72.07; H, 5.26. Found: C, 71.84; H, 5.58.

**$\text{Cp}_2\text{TiAr}(\text{H})\text{C}=\text{C}(\text{H})\text{Bcat}'$  (Ar = *p*-OMe- $\text{C}_6\text{H}_4$ ).** A vial was charged with **2** (39 mg, 0.074 mmol) and cooled to  $-30^\circ\text{C}$ . A cold solution of *p*-methoxystyrene (40 mg, 0.030 mmol) in 10 mL of toluene was added to **2**, and the resulting clear burgundy solution was kept at  $-30^\circ\text{C}$  for 1.5 h. The solution was warmed to room temperature and was concentrated by removal of solvent under reduced pressure. The resulting concentrated solution was layered with pentane and kept at  $-30^\circ\text{C}$  for 8 h. A red solid precipitated and was collected by removing the supernatant by pipet. The solid was washed twice with cold pentane and dried under reduced pressure (53%, 19 mg).  $^1\text{H}$  NMR ( $\text{C}_7\text{D}_8$ ):  $\delta$  6.70 (m, 4 H), 6.42 (s, 5H), 6.12 (s, 5H), 5.60 (d,  $J = 4.1$  Hz, 1H), 4.09 (d,  $J = 4.1$  Hz, 1H), 3.44 (s, 3H), 1.26 (s, 9H).

**Kinetic Studies of Alkene Hydroborations Catalyzed by 2.** Reaction rates were measured by NMR spectroscopy using single-pulse experiments performed every 60 s for 1000 s using an automated program. Rates were determined by integrating the vinyl peaks of *p*-methoxystyrene. To determine the reaction order in alkene, an NMR tube was charged with **2** (2.2 mg, 0.0042 mmol), and the tube was sealed with a septum. The sample was cooled to  $-78^\circ\text{C}$ , and a solution of *p*-methoxystyrene (5.5  $\mu\text{L}$ , 0.042 mmol) and HBcat' (37 mg, 0.21 mmol) in 0.6 mL of  $\text{C}_6\text{D}_6$  was added to the NMR tube by syringe. The tube was shaken to dissolve all the solid without allowing it to warm and was then quickly immersed into the precooled probe ( $-20^\circ\text{C}$ ) of the NMR spectrometer for analysis. The experiment was repeated with 0.21 mmol (5 equiv) of added HBcat' and 0.010, 0.021, 0.063, and 0.083 mmol of added *p*-methoxystyrene. To determine the reaction order in catecholborane, reactions were performed with *p*-methoxystyrene (5.5  $\mu\text{L}$ , 0.042 mmol), **2** (2.2 mg, 0.0042 mmol), and 0.13, 0.27, 0.42, 0.63, and 0.83 mmol of added HBcat'.

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