

True Metal-Catalyzed Hydroboration with Titanium

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Abstract: Dicarboxyltitanocene is an efficient and highly selective catalyst for alkyne hydroborations by catecholborane and dimethyltitanocene is an efficient and highly selective catalyst for alkene hydroborations. These results contrast the hydroboration chemistry with other early transition metal complexes that simply lead to decomposition of catecholborane to form diborane and parallel the hydroboration chemistry of permethylcyclopentadienyl lanthanide complexes. Titanocene dicarbonyl leads to exclusive anti-Markovnikov regiochemistry and to exclusive single additions of catecholborane across alkynes. Dimethyltitanocene leads to predominantly anti-Markovnikov regiochemistry with alkyl-substituted olefins, and exclusive anti-Markovnikov regiochemistry with vinylarenes. Two titanium(III) complexes, $\text{Cp}_2\text{Ti}(\text{H}_2\text{Bcat})$ and $\text{Cp}_2\text{Ti}(\text{Bcat})_2$, were isolated from the reaction mixtures. These Ti(III) complexes, as well as $[\text{Cp}_2\text{TiH}]_2$ and $[\text{Cp}_2\text{TiMe}]_2$, catalyze the addition of catecholborane to olefins more slowly than the titanium(II) and titanium(IV) compounds. These results are rationalized by a σ bond metathesis between catecholborane and titanocene alkene and alkyne complexes that possess metallacyclopropane and metallacyclopropene character as the B–C bond-forming step. This B–C bond-forming step of the catalysis was observed directly in model reactions.

Introduction

Transition metal-catalyzed addition of catecholborane to carbon–carbon multiple bonds^{1,2} has produced chemo-,¹ regio-,^{3–8} diastereo-,^{6–12} and enantioselectivities^{5,13–16} that often complement or improve upon those of uncatalyzed processes, while providing the convenience of handling and workup associated with catecholborane. Initially, the rhodium(I) compound Wilkinson's catalyst was found to catalyze hydroboration, and more recently other Rh(I) and Pd(II) complexes promise useful synthetic methodology^{3,13,17} that has been used in total syntheses.^{18,19} Despite the expectation that the late metal systems follow a simple oxidative addition, migratory insertion, and reductive elimination mechanism, decomposition of the catecholborane into hydrogen, diborane, and a variety of

catecholate-containing main group products occurs with some of these catalysts and hindered olefins.^{20,21} As a result, hydrogenation and uncatalyzed hydroboration can compete with the potentially useful selectivities of metal-catalyzed chemistry.

A number of groups have investigated catalytic hydroboration with early transition metal complexes, in order to reduce the costs of the hydroboration catalysts, to complement the selectivity of the late metal systems, and to seek new catalytic pathways.^{22,23} Although a number of studies have suggested that early transition metals can enhance the rate of addition of catecholborane to alkenes, careful studies of Burgess et al. of the boron-containing products before oxidation to alcohols showed that TiCl_4 , $\text{Ti}(\text{O-Pr})_4$, $\text{Cp}_2\text{Ti}(\text{BH}_4)$, and $(\text{Mesitylene})_2\text{-Nb}$ catalyze decomposition of catecholborane to diborane and B_2Cat_3 ($\text{Cat} = \text{O}_2\text{C}_6\text{H}_4$).^{24–26} As a result, it is diborane that ultimately provides the hydroborated products, and these early transition metal complexes are not “true”²⁷ hydroboration catalysts.²⁸

We report that dicarbonyltitanocene **1** and dimethyltitanocene **2** do catalyze selective additions of catecholborane to both alkenes and alkynes. These catalysts provide essentially

(20) No PPh_3 adducts of catecholborane or decomposition products resulting from them were observed by ¹¹B NMR spectroscopy under our conditions. PPh_3 has been shown to promote degradation of catecholborane, but in THF and at concentrations orders of magnitude greater than those employed in the experiments reported here. Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *Inorg. Chem.* **1993**, *32*, 2175.

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

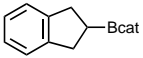
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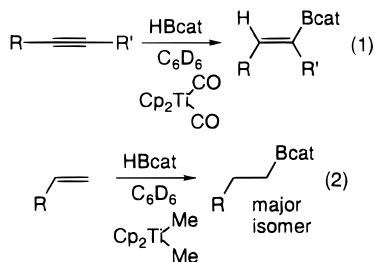
Table 1. Results of Titanocene-Catalyzed Hydroborations

entry no.	substrate	cat.	isolated product(s)	conditions	yield of borane	yield of oxidation prod
1	<i>p</i> -TolC≡CH	4% 1	PhCH=CH(Bcat)	25 °C, 2 h	96%	
2	BuC≡CH	4% 1	BuCH=CH(Bcat)	25 °C, 2 h	97%	
3	PhC≡CPh	4% 1	PhCH ₂ C(O)Ph	25 °C, 2 h		91%
4	MeC≡CPh	4% 1	MeCH ₂ C(O)Ph MeC(O)CH ₂ Ph	25 °C, 2 h		89% 67:33
5	<i>p</i> -TolCH=CH ₂	4% 2	<i>p</i> -TolCH ₂ CH ₂ OH	25 °C, 10 h	96%	89%
6	BuCH=CH ₂	4% 2	BuCH ₂ CH ₂ OH BuCH ₂ (OH)CH ₃	25 °C, 10 h		85% (66:34)
7	(Me)(Bu)C=CH ₂	4% 2	(Me)(Pr)CHCH ₂ Bcat (Me) ₂ (Pr)CBcat	55 °C, 48 h	87% (85:15)	
8		4% 2		25 °C, 10 h		77
9		4% 2		55 °C, 48 h	96%	

quantitative yields of alkyl- and vinylboronate esters with anti-Markovnikov regioselectivity that ranges from good to exclusive. Reaction products resulting from decomposition of catecholborane are absent. The low catalyst cost, the high anti-Markovnikov selectivity with many substrates, and the absence of borane decomposition emulates in some cases and contrasts in others the catalytic hydroboration chemistry of some Rh(I) complexes.

Results and Discussion

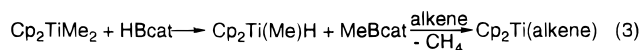
Hydroboration of Alkynes with Cp₂Ti(CO)₂. Results from dicarbonyltitanocene-catalyzed hydroboration of alkynes (eq 1) and dimethyltitanocene-catalyzed hydroboration of alkenes (eq 2) are provided in Table 1. Dicarbonyltitanocene-catalyzed



hydroboration of alkynes was conducted by simply mixing the alkyne with 1.0 equiv of catecholborane and 4 mol % of easily prepared²⁹ and commercially available³⁰ dicarbonyltitanocene **1**. After 2 h at 25 °C, complete conversion of the alkyne had occurred. In all cases a single addition of the borane was observed. Anti-Markovnikov products were formed exclusively with terminal acetylenes. This regioselectivity is higher than that for catecholborane at elevated temperatures in the absence of catalyst (91:9 for phenylacetylene and 93:7 for 1-pentyne),³¹ and is much greater than the poor and variable selectivity observed with Wilkinson's catalyst.²¹ ¹¹B NMR spectroscopy showed that only vinylboronate esters were present in the reaction mixtures. No alkylboranes were formed from multiple hydroborations. No trivinylborane products were formed from uncatalyzed, diborane reaction chemistry. Thus, in contrast to the reactions of the early transition metal systems listed above, the additions of catecholborane to alkynes catalyzed by dicarbonyltitanocene is truly metal-catalyzed hydroboration.

Hydroboration of Alkenes with Cp₂TiMe₂. Hydroboration of alkenes with dicarbonyltitanocene requires the displacement of at least one carbonyl ligand with an alkene, and this ligand substitution is less favorable than displacement by an alkyne. Consistent with this notion, addition of catecholborane to alkenes catalyzed by **1** was markedly slower than addition to alkynes and did not proceed at useful rates unless CO dissociation from **1** was induced photochemically.^{13,23,33} Irradiation of a sealed reaction vessel with a standard medium pressure Hanovia arc lamp led to clean hydroboration chemistry. However, an alternative source of the titanocene fragment was necessary for thermal titanocene-catalyzed alkene hydroborations.

The use of dimethyltitanocene **2** was envisioned to produce a titanocene alkene complex by eq 3, and this method for initiating thermal titanocene-catalyzed hydroboration proved effective. Dimethyltitanocene-catalyzed reactions were con-



ducted by either mixing the alkene and borane with isolated dimethyltitanocene or generating the catalyst *in situ* from commercially available titanocene dichloride and 2 equiv of methylolithium prior to addition of the alkene and borane. Terminal and internal alkenes were hydroborated at room temperature or 55 °C in essentially quantitative yields. Anti-Markovnikov products predominated and were formed exclusively for aryl-substituted alkenes. The anti-Markovnikov selectivity with styrene contrasts the Markovnikov selectivity with rhodium catalysts.³ No vinylboronate esters were observed that would result from β-hydrogen elimination. This selectivity for formation of alkylboronate esters, rather than vinylboronate esters, is remarkable considering that Motry and Smith recently showed that addition of catecholborane to the ethylene complex of permethyltitanocene provides vinylboronate esters.³⁴ Thus, dimethyltitanocene is an effective early metal catalyst for hydroboration of alkenes. It has recently been reported that dimethyltitanocene leads to decomposition of catecholborane and catalyzes additions to alkenes with poor efficiency.²³ The discrepancy between this result and ours is difficult to explain firmly. However, Figure 1 shows crude ¹¹B and ¹H NMR spectra of reaction solutions obtained by catalytic addition of catecholborane to *p*-tolylacetylene and 4-methylstyrene, and

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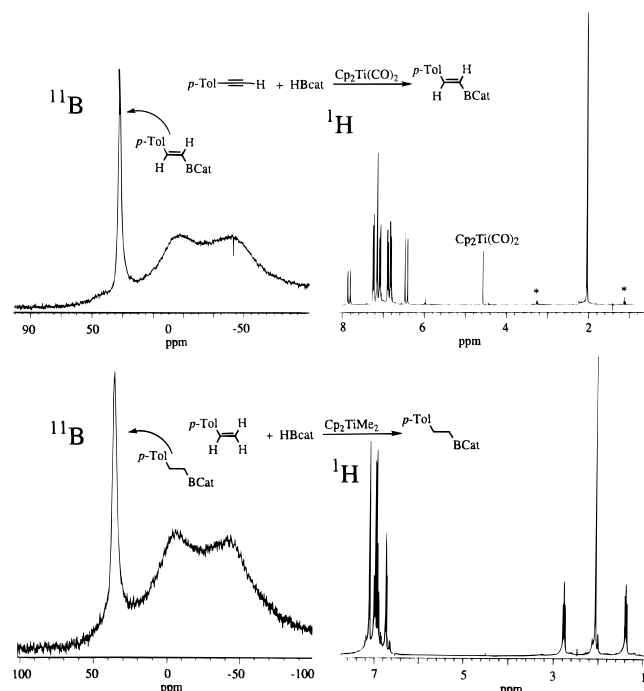
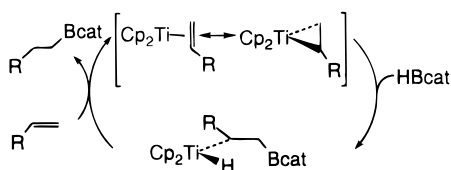


Figure 1. ^{11}B and ^1H NMR spectra of crude reactions of *p*-TolCCH + HBcat catalyzed by **1** (top) and of *p*-TolCHCH₂ + HBcat catalyzed by **2** (bottom). The broad background ^{11}B NMR spectrum is due to the borosilicate glass. NMR spectra were obtained after removing the reaction solvent and dissolving the residue in C₆D₆. Catalyst **1** was observed in the final reaction mixture for alkyne hydroboration, but catalyst **2** decomposed to the paramagnetic **3** over the course of the reaction. The peaks marked with an asterisk were due to traces of ether remaining from the reaction.

Scheme 1



these spectra clearly indicate high yields of alkyl- and vinylborane products without significant decomposition of catecholborane.

Hydroboration of Alkynes with Cp₂TiMe₂. Considering the higher activity of **2** over **1** for catalyzing hydroborations we investigated **2** as a catalyst for alkyne hydroboration. However, it is the greater reactivity of **2** that makes it an inferior alkyne hydroboration catalyst than **1**. Specifically, **2** gives rise to competitive hydroboration of alkenes and alkynes leading to double additions of catecholborane to alkynes. For example, reaction of 1-hexyne with catecholborane catalyzed by **2** gave between 15% and 45% of the double addition product under various reaction conditions. Further the regioselectivity was inferior to that of **1**. Reactions of the same alkynes with catecholborane catalyzed by **2** gave between 8% and 15% of the Markovnikov product.

Mechanistic Considerations. A proposed mechanism for additions to alkenes is provided in Scheme 1, and an analogous mechanism for additions to alkynes is proposed, since it is known that alkynes reversibly displace a single carbonyl of **1** at room temperature.³⁵ The mechanism is likely to proceed by σ -bond metathesis between catecholborane and one Ti–C bond of a titanocene alkene or alkyne complex that is known to adopt significant metallacyclopropane or -propene character due to

the strong backbonding ability of d² metals.^{35–37} The anti-Markovnikov selectivity is consistent with addition of the B–H bond of catecholborane to the less hindered Ti–C bond. A detailed account of stoichiometric σ -bond metathesis involving a ruthenium alkyl and catecholborane,³⁸ other similar stoichiometric exchanges,^{20,39,40} and the proposed but not directly observed σ -bond metathesis in lanthanide-catalyzed hydroboration by Harrison and Marks²⁸ led us to consider that mechanisms including a σ -bond metathesis step could lead to catalytic hydroborations, particularly since such B–C bond formation occurred in high yield with no evidence for decomposition of borane.

Mechanistic alternatives to σ -bond metathesis include pathways involving oxidative addition of catecholborane to Ti(II) and formation of a hydrido boryl complex of titanocene as either a 16-electron intermediate or an 18-electron alkene complex. However, no group IV boryl complexes or 16-electron d⁰ boryl complexes of any metal have been isolated, few d⁰ alkene complexes are known, and we found that dicarbonyltitanocene does not react with catecholborane under thermal or photochemical conditions that are similar to those of the catalysis. Further, Binger et al. noted that the addition of diethylborane to Cp₂Ti(alkyne)(PMe₃) led to insertion of the borane B–H bond into one of the Ti–C bonds,⁴¹ a reaction that is analogous to the B–C bond-forming step of our proposed mechanism. The alkyl-substituted boron center of this reaction product maintained a strong B–H interaction, apparently preventing reductive elimination. With the π -donating catecholate group in the compounds of our work, the B–H interaction would be weaker⁴² and would lead to a more standard vinyl hydride intermediate that can regenerate the titanium alkyne complex after reductive elimination.

Additional alternative mechanisms would include catalysis by Ti(III) complexes, similar to those believed to be involved in hydrogenation and hydrosilylation by titanocene complexes.⁴³ However, our studies suggest that Ti(III) complexes do not catalyze the hydroboration reactions or do so slowly at best. Ti(III) complexes generated by addition of 2 equiv of BuLi to Cp₂TiCl₂ or by addition of 1 equiv of BuLi to [Cp₂TiCl]₂ catalyze hydroboration, but much more slowly than initial rates of reactions catalyzed by **1** or **2**. Thus, Ti(III) alkyl species are unlikely to be the most active catalyst in the system, and it appears likely that much of the chemistry employs Ti(II) and Ti(IV). Reaction via Ti(III) may be occurring after longer reaction times.

Although we have not conducted a full mechanistic study, we have obtained data that support the chemistry in eq 3 and Scheme 1. First, the reaction of catecholborane with **2** in the absence of alkene forms methylcatecholborane, which was identified by ^{11}B and ^1H NMR spectroscopy, and methane, which was identified by its ^1H NMR chemical shift of δ 0.14. Under these conditions that lack alkene to trap the resulting titanium fragment, multiple transition metal products were formed. In addition, we have observed that Cp₂Ti(PhC≡CPh)-

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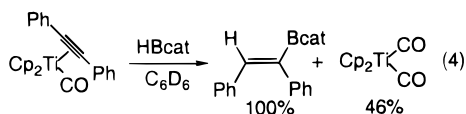
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(CO) does react with catecholborane immediately at room temperature to form dicarbonyltitanocene and the vinylboronate ester CatB(Ph)C=CHPh as shown in eq 4. Reaction yields were



measured by ^1H NMR spectroscopy with an internal standard and the dicarbonyltitanocene was formed in 46% yield based on titanium (50% is the maximum yield for the amount of CO present) and the vinylboronate ester was formed in quantitative yield. No ^{11}B NMR resonances were observed that would indicate formation of a stable intermediate with the boron interacting with a titanium hydride.

Isolation of Two Forms of Deactivated Catalyst. Further evidence against Ti(III) complexes being important for the catalysis is the isolation of the titanocene catalyst in two sequential deactivated forms. Room temperature reactions of alkyl-substituted alkenes became violet and eventually turned blue. Under conditions of high catalyst loading, the violet complex crystallized from the benzene reaction solvent as needles. Recrystallization from ether gave material suitable for an X-ray diffraction study that showed its structure to be $\text{Cp}_2\text{-Ti(H}_2\text{Bcat)}$ (**3**). Apparently the presence of alkene is necessary to generate the additional hydride in **3**, since addition of HBcat to Cp_2TiMe_2 did not provide **3**, as noted above.

^1H NMR spectra for **3** were broad, but two aromatic resonances could be observed at room temperature at δ 8.3 and 7.2. The EPR spectrum showed a g -value of 1.990, consistent with those of other Ti(III) complexes, including the 2.004 value of $\text{Cp}_2\text{Ti(BH}_4\text{)}$.⁴⁴ No hyperfine coupling to the bridging hydride ligands in **3** was observed. The absence of coupling was expected since no ligand hyperfine was observed in the previous EPR spectrum of $\text{Cp}_2\text{Ti(BH}_4\text{)}$.⁴⁴ This complex is a structural analog of our previously communicated $\text{Cp}_2\text{Nb(H}_2\text{Bcat)}$ that showed unusual structural features as determined by isotope perturbation. Complete structural information on **3** and data concerning a mechanism for its formation will be reported elsewhere.

Compound **3** catalyzed the reaction, but reactions initiated with **3** occurred much more slowly than reactions initiated with **2**. For example, reaction of hexane and catecholborane catalyzed by **2** were complete after 8 h at 0 °C, while the same reaction employing **3** showed less than 5% conversion at that time. Reactions were run in an ice bath to ensure that the exothermicity of catalyst generation from **2** did not account for the faster reaction of **2** relative to **3**. These data support the proposal that the Ti(III) oxidation state is not part of the dominant catalytic pathway.

With more typical catalyst loadings the purple compound remained in solution and eventually a blue crystalline complex **4** was deposited. The identity of this complex was shown by X-ray diffraction studies to be the Ti(III) borate $\text{Cp}_2\text{Ti(BCat}_2\text{)}$. ^1H NMR spectra of this complex were broad, but the aromatic protons were observed at δ 5.9 and 7.3. The EPR spectrum of this complex again showed a g -value, 1.979, that was consistent with similar Ti(III) complexes and most resembled that of $\text{Cp}_2\text{-Ti(O}_2\text{CH)}$, $\text{Cp}_2\text{-Ti(OCMe}_3\text{)}$, and $\text{Cp}_2\text{-Ti(BH}_4\text{)}$.⁴⁵ It is likely that **4** is produced by disproportionation of **3** into **4** and BH_4^- , but firm information awaits further study. Compound **4** not only

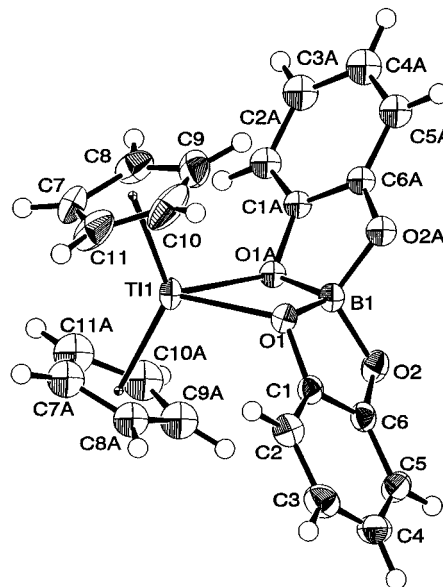


Figure 2. ORTEP drawing of **3**.

was isolated from catalytic reaction solutions but was synthesized in nearly quantitative yield by the reaction of Cp_2TiMe_2 with excess catecholborane (4 equiv) in the presence of a small amount of isoprene. Reaction in the absence of any olefin did not lead to formation of a single titanium species (*vide supra*), but reaction with only 1/3 equiv of isoprene gave high yields of **4**. Surprisingly, no tri- or tetraalkylborane was observed in the ^1H NMR spectrum of this crude reaction mixture.

However, it was clear again that complex **4** did not lie on the catalytic cycle of the hydroboration process. Reactions employing compound **4** as catalyst proceeded even more slowly than those involving **3**, further supporting the proposal that the Ti(III) oxidation state is not part of the catalytic pathway. Nevertheless, EPR spectra of the reaction mixtures collected before complete conversion of catecholborane showed that both **3** and **4** were present, suggesting that catalyst decomposition competes with catalytic hydroboration. It is interesting to note that rhodium(I) compounds containing η^6 -bound Bcat_2 are catalytically active,³ in contrast to the Ti(III) reported here.

Structure of $\text{Cp}_2\text{Ti(BCat}_2\text{)}$ (4**).** Compound **4** is an uncommon example of a transition metal tetraalkoxy or -aryloxyborate, and possesses some unusual structural features such as a small O—M—O angle and long Ti—O distances. An ORTEP drawing of **4** is provided in Figure 2; crystal parameter, bond angles, and bond distances are provided in Tables 2–4. Although some similar nickel Bcat_2 compounds proposed to have an O-bound borate anion,^{46,47} the only previous structurally characterized metal tetraalkoxyborates are a lanthanum tetraalkoxyborate,⁴⁸ the silver $\text{B(OTeF}_5\text{)}_4$ complex with coordinated CO ,⁴⁹ and a silver complex of the borate antibiotic aplasmomycin.⁵⁰ The Cp(centroid)—Ti—Cp(centroid) angle of 134.0° is typical for $\text{Cp}_2\text{Ti(III)}$ complexes,^{51–54} as is the Cp(centroid)—Ti distance

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Table 2. Crystal and Experimental Parameters for **4**

A. Crystal Data		
empirical formula	C ₂₂ H ₁₈ O ₄ BTi	
formula wt	405.09	
crystal color/habit	bright blue prism	
crystal dimensions (mm)	0.22 × 0.27 × 0.34	
crystal system	orthorhombic	
no. of reflns used for unit cell determination (2θ range)	25 (8.0–19.0°)	
lattice parameters		
<i>a</i> (Å)	11.410(2)	
<i>b</i> (Å)	8.910(2)	
<i>c</i> (Å)	18.406(7)	
<i>V</i> (Å ³)	1871(1)	
space group	<i>Pbcn</i> (No. 60)	
<i>Z</i> value	4	
<i>D</i> _{calc} (g/cm ³)	1.438	
F000	836	
μ(Mo Kα) (cm ⁻¹)	4.75	
B. Intensity Measurements		
diffractometer	Enraf-Nonius CAD-4	
radiation	Mo Kα (λ = 0.71069 Å)	
temperature (°C)	-90	
attenuator	Zr foil (factor = 20.4)	
take-off angle (deg)	2.8	
detector aperture (mm)	2.0–2.5 hor./2.0 vert.	
crystal-to-detector distance (cm)	21	
scan type	ω-2θ	
scan rate (deg/min (in ω))	1.0–16.0	
scan width	(0.67 + 0.85 tan θ)°	
2θ _{max} (deg)	52.5	
total no. of reflns meas	2188	
corrections	Lorentz-polarization	
C. Structure Solution and Refinement		
structure solution	direct method	
refinement	full-matrix least-squares	
function minimized	Σ _w (F _o - F _c) ²	
least-squares weights	4F _o ² /σ ² (F _o ²)	
<i>p</i> -factor	0.03	
anomalous dispersion	all non-hydrogen atoms	
no. of observations (<i>I</i> > 3.00σ(<i>I</i>))	1545	
no. of variables	128	
reflection/parameter ratio	12.07	
residuals: <i>R</i> ; <i>R</i> _w	0.036; 0.053	
goodness-of-fit indicator	2.40	
max shift/error in final cycle	0.00	
max peak in final diff. map (e/Å ³)	0.27	
min peak in final diff. map (e/Å ³)	-0.39	

Table 3. Intramolecular Distances Involving the Non-Hydrogen Atoms for **4**^a

Ti1-O1	2.236(1)	O2-C6	1.355(2)
Ti1-O1	2.236(1)	O2-B1	1.459(2)
Ti1-C7	2.351(2)	C1-C2	1.368(3)
Ti1-C7	2.351(2)	C1-C6	1.391(3)
Ti1-C8	2.334(2)	C2-C3	1.398(3)
Ti1-C8	2.334(2)	C3-C4	1.390(3)
Ti1-C9	2.351(2)	C4-C5	1.395(3)
Ti1-C9	2.351(2)	C5-C6	1.382(3)
Ti1-C10	2.391(2)	C7-C8	1.387(3)
Ti1-C10	2.391(2)	C7-C11	1.402(4)
Ti1-C11	2.382(2)	C8-C9	1.405(3)
Ti1-C11	2.382(2)	C9-C10	1.392(4)
O1-C1	1.393(2)	C10-C11	1.376(4)
O1-B1	1.504(2)		

^a Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

of 2.04 Å. However, the O-Ti-O angle of 63.77(6) Å is much smaller than the optimal angle of 85° determined by EHMO

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Table 4. Intramolecular Bond Angles Involving the Non-Hydrogen Atoms for **4**^a

O1-Ti1-O1	63.77(6)	C7-Ti1-C10	56.44(8)
O1-Ti1-C7	135.94(7)	C7-Ti1-C10	112.60(9)
O1-Ti1-C7	124.53(7)	C7-Ti1-C11	34.45(9)
O1-Ti1-C8	117.95(7)	C7-Ti1-C11	81.75(9)
O1-Ti1-C8	90.98(7)	C7-Ti1-C8	113.05(9)
O1-Ti1-C9	84.39(7)	C7-Ti1-C8	34.45(8)
O1-Ti1-C9	83.95(7)	C7-Ti1-C9	136.42(8)
O1-Ti1-C10	79.82(6)	C7-Ti1-C9	57.09(8)
O1-Ti1-C10	111.46(8)	C7-Ti1-C10	112.60(9)
O1-Ti1-C11	108.19(8)	C7-Ti1-C10	56.44(8)
O1-Ti1-C11	140.68(7)	C7-Ti1-C11	81.75(9)
O1-Ti1-C7	124.53(7)	C7-Ti1-C11	34.45(9)
O1-Ti1-C7	135.94(7)	C8-Ti1-C8	146.8(1)
O1-Ti1-C8	90.98(7)	C8-Ti1-C9	34.89(9)
O1-Ti1-C8	117.95(7)	C8-Ti1-C9	152.70(9)
O1-Ti1-C9	83.95(7)	C8-Ti1-C10	57.19(8)
O1-Ti1-C9	84.39(7)	C8-Ti1-C10	118.57(9)
O1-Ti1-C10	111.46(8)	C8-Ti1-C11	57.40(8)
O1-Ti1-C10	79.82(6)	C8-Ti1-C11	99.96(9)
O1-Ti1-C11	140.68(7)	C8-Ti1-C9	152.70(9)
O1-Ti1-C11	108.19(8)	C8-Ti1-C9	34.89(9)
C7-Ti1-C7	81.6(1)	C8-Ti1-C10	118.57(9)
C7-Ti1-C8	34.45(8)	C8-Ti1-C10	57.19(8)
C7-Ti1-C8	113.05(9)	C8-Ti1-C11	99.96(9)
C7-Ti1-C9	57.09(8)	C8-Ti1-C11	57.40(8)
C7-Ti1-C9	136.42(8)	C9-Ti1-C9	166.3(1)
C9-Ti1-C10	34.14(9)	O2-C6-C5	127.8(2)
C9-Ti1-C10	148.69(9)	C1-C6-C5	120.4(2)
C9-Ti1-C11	56.73(9)	Ti1-C7-C8	72.1(1)
C9-Ti1-C11	134.56(9)	Ti1-C7-C11	74.0(1)
C9-Ti1-C10	148.69(9)	C8-C7-C11	108.6(2)
C9-Ti1-C10	34.14(9)	Ti1-C8-C7	73.4(1)
C9-Ti1-C11	134.56(9)	Ti1-C8-C9	73.2(1)
C9-Ti1-C11	56.73(9)	C7-C8-C9	107.1(2)
C10-Ti1-C10	167.2(1)	Ti1-C9-C8	71.9(1)
C10-Ti1-C11	33.51(9)	Ti1-C9-C10	74.5(1)
C10-Ti1-C11	133.7(1)	C8-C9-C10	107.9(2)
C10-Ti1-C11	133.7(1)	Ti1-C10-C9	71.3(1)
C10-Ti1-C11	33.51(9)	Ti1-C10-C11	72.9(1)
C11-Ti1-C11	100.5(1)	C9-C10-C11	108.6(2)
Ti1-O1-C1	126.3(1)	Ti1-C11-C7	71.6(1)
Ti1-O1-B1	96.4(1)	Ti1-C11-C10	73.6(1)
C1-O1-B1	106.0(1)	C7-C11-C10	107.7(2)
C6-O2-B1	107.5(1)	O1-B1-O1	103.4(2)
O1-C1-C2	128.0(2)	O1-B1-O2	104.91(7)
O1-C1-C6	109.1(2)	O1-B1-O2	115.93(7)
C2-C1-C6	122.9(2)	O1-B1-O2	115.93(7)
C1-C2-C3	116.8(2)	O1-B1-O2	104.91(7)
C2-C3-C4	121.0(2)	O2-B1-O2	111.8(2)
C3-C4-C5	121.3(2)	C4-C5-C6	117.6(2)
O2-C6-C1	111.8(2)		

^a Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

calculations for d¹ Cp₂ML₂ complexes.⁵⁵ Most other compounds with titanium-oxygen bonds, either dative or covalent, have angles that are closer to this value of 85°. For example, [Cp₂Ti(THF)₂]⁺ has angles of 77–83° for three independent cations,⁵³ [Cp₂Ti(THF)(NCMe)]⁺ has an O-Ti-N angle of 84.2(2) Å,⁵⁴ and [Cp₂Ti(acetone)(THF)]⁺ has angles of 76.9° and 78.6°. The dimeric [Cp₂Ti(OMe)]₂ has a smaller angle (72.2(2)°)⁵⁶ than these monomeric dative complexes, while geometrically constrained carboxylate (60.38(8)°)⁵⁷ and carbonate (61.3(1)°)⁵⁸ complexes are more similar in their O-Ti-O angles. The small O-Ti-O angle in **4** is accompanied by long Ti-O bonds of 2.236(1) Å. These distances are longer than

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Table 5. Distances and Angles Involving the Cp Centroid

Cp–Ti	2.04
Cp–Ti–Cp _a	134.0
Cp–Ti–O1	106.0
Cp–Ti–B1	113.0

those of the covalent methoxide (2.065(2) Å) or either Ti–O distances of the carbonate (2.128(3), 2.183(2) Å) or carboxylate (2.163(2), 2.162(2) Å). These distances are closest to THF complexes (2.17–2.21 Å), a DME complex (2.121(4) and 2.109-(4) Å),⁵⁹ and the center oxygen of an anhydride complex (2.205-(9) Å),⁶⁰ but are even slightly longer than these. As one would expect, the Ti–B distance is much longer than that in Cp₂Ti–(BH₄).⁶¹

Summary. One method for creating a metal–carbon σ bond from a metal complex and an alkene is by alkene insertion reactions. This transformation is proposed to be important in Rh(I) and Cp*₂LnR catalyzed hydroborations, and may be important in the hydroborations catalyzed by Cp₂Zr(H)(Cl).²² Alternatively, coordination of an alkene to an electron-rich metal center creates a complex with metal–carbon σ bond character in the form of a metallacyclopropane. We have shown that early transition metal complexes are capable of catalyzing hydroboration reactions as a result of their electronic ability to complex alkenes in a manner that creates two metal–carbon σ bonds. The presence of these σ bonds provides a pathway for catalytic hydroboration that does not involve alkene insertions and is, therefore, distinct from both rhodium complexes and f-block complexes.

We are currently investigating in more detail the chemoselectivity of this titanocene chemistry and the factors that control it. Since the inexpensive, rigid, and sterically demanding titanocene catalysts provide selectivity that complements or rivals in some cases the best rhodium systems, compounds **1** and **2** are likely to find applications in diastereoselective borane additions. The high enantioselectivities obtained with chiral metallocenes in other reactions suggest their potential in asymmetric hydroborations. We plan to investigate these applications in the future.

Experimental Section

General. All reactions were conducted under a nitrogen atmosphere in a drybox or by standard Schlenk techniques. Cp₂Ti(CO)₂ and TiCp₂Me₂ were prepared according to literature procedures.^{29,62} All alkynes and alkenes were dried over CaH₂ and were vacuum transferred prior to use. Catecholborane was purchased from Aldrich and was purified by distillation under reduced pressure. ¹³C, ¹¹B, ¹H, and COSY NMR spectra were obtained on GE QE300 and GE Ω -300 spectrometers. ¹¹B NMR chemical shifts are recorded in units of parts per million relative to the external standard BF₃·Et₂O. ¹H NMR chemical shifts are recorded in parts per million relative to tetramethylsilane. ESR spectra were recorded on a Varian E-LINE spectrometer operating at Q band and 25 °C. The *g*-value was referenced to DPPH with a *g*-value of 2.0037 ± 0.0002. The concentrations of toluene solution for EPR were prepared in 10–50 μ M. GC and GC/MS measurements were conducted on a Hewlett Packard 5890 Series II gas chromatograph.

Preparation of *p*-Tol-CH=CH(Bcat). A 25-mL screw-topped vial was charged with *p*-TolCCH (1.25 mL, 9.57 mmol), Cp₂Ti(CO)₂ (89 mg, 0.38 mmol), and ethyl ether (2 mL). To the rapidly-stirred solution was added catecholborane (1.02 mL, 9.61 mmol) by syringe and the vial was sealed with a cap. The solution was allowed to react for 2 h at room temperature. Storage in a –35 °C freezer for 1 h was followed

by fast filtration through a fritted glass funnel and washing with cool pentane (1 mL). This afforded pure crystalline product. Yield: 2.19 g, 96%. ¹¹B NMR (C₆D₆) δ 32.6; ¹³C NMR (C₆D₆) δ 152.2, 148.7, 139.5, 134.5, 129.4, 127.5, 122.6, 112.4, 21.0; ¹H NMR (C₆D₆) δ 7.87 (1H, d, *J* = 18.5 Hz), 7.30 (2H, d, *J* = 7.8 Hz), 7.12 (2H, m), 6.93 (2H, d, *J* = 7.8 Hz), 6.89 (2H, m), 6.48 (1H, d, *J* = 18.5 Hz).

Preparation of BuCH=CH(Bcat). A procedure analogous to that used to prepare *p*-Tol-CH=CH(Bcat) was followed starting with BuCCH (1.12 mL, 9.58 mmol), HBcat (1.02 mL, 9.61 mL), and Cp₂Ti(CO)₂ (89 mg, 0.38 mmol). The pure product⁶³ was obtained by vacuum condensation of **2** (35 °C/10^{–3} Torr) onto a cold finger (–78 °C). Yield: 1.87 g, 97%.

Preparation of PhCH₂C(O)Ph. The vinylboronate ester was prepared by a procedure analogous to that used to prepare *p*-Tol-CH=CH(Bcat), but starting with PhCCPh (1.17 g, 6.57 mmol), HBcat (0.703 mL, 6.62 mmol), and Cp₂Ti(CO)₂ (60 mg, 0.256 mmol). The product was crystallized from Et₂O solution at –35 °C, washed with cold pentane, and dried under reduced pressure. Yield: 1.84 g, 94%. ¹¹B NMR (C₆D₆) δ 32.6; ¹³C NMR (C₆D₆) δ 148.7, 145.9, 139.6, 136.5, 130.3, 128.9, 128.6, 128.3, 128.0, 126.7, 122.6, 112.3; ¹H NMR (C₆D₆) δ 7.88 (1H, s), 7.3–7.05 (8H, m), 7.02 (2H, m), 6.90 (2H, m), 6.78 (2H, m). Phenylacetophenone was obtained after treating the borane with NaOH/H₂O₂ in THF for 10 h. Upon removal of THF the product was extracted with pentane (3 × 15 mL), washed with water, and dried with MgSO₄. Removal of the solvent under reduced pressure afforded pure product. Yield: 1.18 g, 91%.

Preparation of PhC(O)CH₂Me and PhCH₂C(O)Me. The procedure was similar to that used to prepare PhCH₂C(O)Ph, but starting with MeCCPh (1.21 mL, 9.58 mmol), HBcat (1.02 mL, 9.61 mmol), and Cp₂Ti(CO)₂ (89 mg, 0.38 mmol). The major vinylboronate ester intermediate PhCH=C(BCat)Me obtained by the hydroboration was isolated by recrystallization of the products from pentane. Yield: 1.45 g, 64%. ¹¹B NMR (C₆D₆) δ 32.6; ¹³C NMR (C₆D₆) δ 148.7, 145.3, 137.4, 129.6, 128.1, 127.8, 122.5, 112.3, 15.3; ¹H NMR (C₆D₆) δ 7.80 (1H, s), 7.4–7.0 (7H, m), 6.85 (2H, m), 2.15 (3H, s). The oxidation of the crude boronate esters provided 1.14 g of the ketone mixture in 89% yield.

Preparation of *p*-TolCH₂CH₂Bcat and *p*-TolCH₂CH₂OH. Into a vial sealed with a rubber septum was placed *p*-TolCH=CH₂ (1.32 mL, 9.58 mmol), Cp₂TiMe₂ (80 mg, 0.38 mmol), and benzene (3 mL). To this solution was added catecholborane (1.16 mL, 10.4 mmol) very slowly by syringe with stirring. Gas evolution was observed and was completed after about 20 min. The resulting solution was allowed to react for an additional 1.5 h at room temperature. Upon removal of the solvent and sublimation at 85 °C/10^{–3} Torr, off-white solid alkylboronate ester was obtained. Yield: 2.19 g, 96%. ¹¹B NMR (C₆D₆) δ 35.6; ¹³C NMR (C₆D₆) δ 148.6, 140.7, 135.0, 129.2, 127.8, 122.5, 112.3, 29.4, 20.8; ¹H NMR (C₆D₆) δ 1.50 (2H, t, *J* = 8.1 Hz), 2.17 (3H, s), 2.88 (2H, t, *J* = 8.1 Hz), 6.85 (2H, m), 7.07 (6H, m). The oxidation procedure was similar to that for PhCH₂C(O)Ph, but Et₂O was used instead of THF solvent. The alcohol product was purified by vacuum distillation at 50 °C/10^{–3} Torr onto a cold finger. Yield: 1.16 g, 89%.

Preparation of BuCH₂CH₂OH and BuCH(OH)CH₃. The preparation was analogous to that used to prepare *p*-TolCH₂CH₂OH, but starting with 1-hexene (1.21 mL, 9.58 mmol), HBcat (1.16 mL, 10.3 mmol), and Cp₂TiMe₂ (80 mg, 0.38 mmol). The alkylboronate ester was separated from the catalyst by condensation (85 °C/10^{–3} Torr) onto a cold finger (–78 °C) before oxidation. Yield of alcohol: 0.832 g, 85%.

Preparation of (Me)(Pr)CHCH₂Bcat and (Me)₂(Pr)CBcat. The alkylboronate ester was obtained by a similar procedure to that used to prepare the intermediate boronate ester *p*-TolCH₂CH₂Bcat, but starting with 2-methyl-1-pentene (1.72 mL, 14.0 mmol), HBcat (1.10 mL, 10.4 mmol), and Cp₂TiMe₂ (80 mg, 0.38 mmol) and conducting the reaction at 55 °C for 48 h. Yield: 1.85 g, 87%. ¹¹B NMR (C₆D₆) δ 36.2. ¹³C NMR (C₆D₆) δ (Me)(Pr)CHCH₂Bcat: 148.4, 122.3, 112.1, 41.6, 29.0, 22.1, 20.4, 14.0. ¹³C NMR (C₆D₆) δ (Me)₂(Pr)CBcat: 148.4, 122.4, 112.3, 43.9, 24.8, 19.7, 14.7. ¹H NMR (C₆D₆) δ (Me)(Pr)CHCH₂Bcat: 7.0 (2H, m), 6.8 (2H, m), 1.9 (1H, m), 1.4–0.9 (4H, m),

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0.9 (3H, d), 0.9–0.7 (5H, m). ^1H NMR ($\text{Me}_2(\text{Pr})\text{CBcat}$): 7.0 (2H, m), 6.8 (2H, m), 1.5–1.1 (4H, m), 1.1 (6H, s), 0.85–0.75 (3H, t). From this reaction solution was deposited blue crystalline **4** that was washed with ether and which was suitable for X-ray structural characterization.

Preparation of Cyclopentanol. The procedure was analogous to that used to prepare $\text{BuCH}_2\text{CH}_2\text{OH}$, but starting with cyclopentene (0.848 mL, 9.58 mmol), HBcat (1.16 mL, 10.3 mmol), and Cp_2TiMe_2 (80 mg, 0.38 mmol). Yield of alcohol: 0.636 g, 77%.

Preparation of 2-Indenylboronate Ester. The alkylboronate ester was obtained by a procedure analogous to that used to obtain $p\text{-TolCH}_2\text{-CH}_2\text{Bcat}$, but starting with indene (1.13 mL, 9.58 mmol), HBcat (1.16 mL, 10.3 mmol), and Cp_2TiMe_2 (80 mg, 0.38 mmol) and conducting the reaction at 55 °C for 48 h. The highly crystalline, white boronate ester of indene was isolated by extraction with ether and removal of solvent. Yield: 2.16 g, 96%. ^{11}B NMR (C_6D_6) δ 35.0; ^{13}C NMR (C_6D_6) δ 148.5, 143.5, 126.2, 124.2, 122.4, 112.2, 35.0; ^1H NMR (C_6D_6) δ 7.04 (4H, m), 6.95 (2H, m), 6.75 (2H, m), 3.02 (4H, m), 2.02 (1H, pentet).

Preparation of $\text{Cp}_2\text{Ti}(\text{H}_2\text{Bcat})$ (3**).** To a solution of Cp_2TiMe_2 (146 mg, 0.70 mmol) in toluene (1 mL) was added slowly a solution of 1-hexene (240 μL , 1.92 mmol) and HBcat (240 μL , 2.25 mmol) in toluene (1 mL). After the addition, the reaction vial was closed and stored in a –35 °C freezer for 3 h. The mother liquor was removed, and the resulting violet needles were washed with pentane and dried under reduced pressure. Yield: 130 mg, 62%. EPR (C_7H_8): $g = 1.990$. IR (C_7H_8): 1778 (broad), 1840 (broad). ^1H NMR (C_6D_6) δ 8.1, 7.2 (broad).

Preparation of $\text{Cp}_2\text{Ti}(\text{Cat}_2\text{B})$ (4**).** Into a vial sealed with a rubber septum was placed isoprene (13 μL , 0.13 mmol), Cp_2TiMe_2 (68.5 mg, 0.33 mmol), and benzene (0.5 mL). Catecholborane (140 μL , 1.32 mmol) was added to this mixture slowly by syringe with stirring. This resulting solution was allowed to react at 80 °C for 1 h. After removal of volatile species, the residue was washed with pentane and dried under reduced pressure to provide 131 mg of crude product **3** that was recrystallized from Et_2O to produce blue crystalline **3**. Yield: 104 mg, 78%. EPR (C_7H_8): $g = 1.979$.

X-ray Crystallographic Studies. Bright blue prisms of **3** were immersed in Paratone N oil (Exxon) and a crystal having the approximate dimensions of $0.22 \times 0.27 \times 0.34$ mm was mounted on a glass fiber and placed into the N_2 cold stream of the diffractometer. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated $\text{Mo K}\alpha$ radiation.

Cell constants and an orientation matrix for data collection obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $8.0 < 2\theta < 19.0^\circ$ corresponded to an orthorhombic cell with the crystal parameters in Table 1. Based on the systematic absences of $0kl$: $k = 2n + 1$; $h0l$: $l = 2n + 1$; $hk0$: $h + k = 2n + 1$ and the successful solution and refinement of the structure the space group was determined to be $Pbcn$ (No. 60). In this space group, the molecule is located on a crystallographic 2-fold axis.

Diffraction data were collected at -90 ± 1 °C using the ω - 2θ technique to a maximum 2θ value of 52.5° with a take-off angle of 2.8° . Scans of $(0.67 + 0.85 \tan \theta)^\circ$ were made at speeds ranging from 1.0 to 16.0 deg/min (in ω). Moving-crystal moving-counter background measurements were made by scanning an additional 25% above and below the scan range. The counter aperture consisted of a variable horizontal slit with a width ranging from 2.0 to 2.5 mm and a vertical slit set to 2.0 mm. The diameter of the incident beam collimator was

0.7 mm and the crystal to detector distance was 21 cm. For intense reflections the attenuator was automatically inserted in front of the detector.

A total of 2188 reflections was collected. The intensities of three representative reflections which was measured after every 60 min of X-ray exposure time remained constant throughout data collection indicating crystal and electronic stability. No decay correction was applied. The linear absorption coefficient for $\text{Mo K}\alpha$ is 4.8 cm^{-1} . Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions. The final cycle of full-matrix least-squares refinement was based on 1545 observed reflections ($I > 3.00\sigma(I)$) and 128 and converged (the largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.036$$

$$R_w = [(\sum w(|F_o| - |F_c|)^2) / \sum |F_o|]^{1/2} = 0.053$$

The standard deviation of an observation of unit weight was 2.40. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$ reflection order in data collection, $\sin(\theta/l)$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.27 and $-0.39 \text{ e}^-/\text{\AA}^3$. Neutral atom scattering factors were taken from Cromer and Waber.⁶⁴ Anomalous dispersion effects were included in F_{calc} ; the values for $\Delta f'$ and $\Delta f''$ were also those of Cromer and Waber.⁶⁵ All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corp.

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Supporting Information Available: Tables of positional parameters, $B(\text{eq})$ and U values, Cartesian coordinates, intramolecular bond angles involving the hydrogen atoms, and Torsion or conformation angles for **3** (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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