New Homogeneous Rhodium Catalysts for the Regioselective Hydroboration of Alkenes†

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Abstract: Multinuclear (^{1}H, ^{11}B, ^{13}C, ^{19}F, and ^{31}P) NMR spectroscopy was used to monitor primary products from transition metal-catalyzed addition of catecholborane (HBcat) to a variety of alkenes. Hydroboration of vinylarenes (indene, vinylnaphthalene, and X-C_6H_4-CH=CH_2, where X = *p*-OMe, *p*-F, *p*-Cl, and *m*-F) with HBcat, employing [Rh(η^3-2-Me-allyl){($Pr^i_2PCH_2$)$_2$}] (**9**) as catalyst precursor, proceeded with excellent activity and regioselectivity (>99%) in favor of the corresponding internal boronate ester. Analogous hydroboration reactions carried out in the presence of [Rh(COD){($Ph_2PCH_2CH_2$)$_2$}]BF_4 (**11**) (COD = 1,5-cyclooctadiene) or Wilkinson's catalyst, [RhCl(PPh_3)$_3$] (**1**), also gave internal boronate esters with regioselectivities comparable to those of **9**. With **1**, unlike **9** and **11**, however, small amounts (ca. 5%) of hydrogenation products were observed consistently. With (*E*)-1-phenylpropene, **9** and **11** again gave internal boronate ester (>99%), whereas **1** gave a 70:30 mixture of internal:terminal boronate esters, with 5% *n*-propylbenzene as a side product. The effect of varying the chelating bis(phosphine) in [Rh(η^3-2-Me-allyl)(P_2)] was examined for catalyzed hydroborations of 2-phenylpropene. Higher chemical yields and Markovnikov selectivities were observed for arylphosphines compared with corresponding bulky alkylphosphines. Unlike cationic [Rh(diene)(P_2)]$^+$ catalyst precursors, hydroborations of aliphatic alkenes using **9** proceeded with complete regiocontrol to give terminal alkylboronate esters. Hydroboration of 2,3-dimethylbut-2-ene with HBcat was also catalyzed by **9** and **11**; complex **1** failed to catalyze hydroboration of this sterically demanding substrate. Complex **9** reacts with excess HBcat to form zwitterionic [Rh(η^6-catBcat){($Pr^i_2PCH_2$)$_2$}] (**12**), which is proposed to be the resting state of the active hydroboration catalyst. In situ monitoring of catalytic reactions using allylrhodium precursors by ^{31}P{^{1}H} NMR spectroscopy showed that only the zwitterionic species were present *in observable quantities* at any time during or after completion of catalysis. Conversely, hydroborations using **11** gave several phosphinorhodium complexes, leading eventually to catalyst decomposition. The new zwitterionic catalysts can also be generated conveniently from [Rh(acac)(η-C_2H_4)$_2$] (acac = acetylacetonate), phosphine ligands, and HBcat.

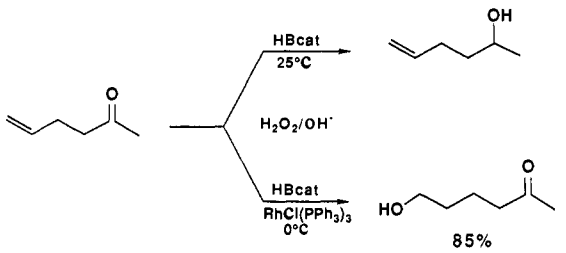
Introduction

Addition of B-H bonds to carbon-carbon multiple bonds was first introduced and developed by Brown in 1956.[1] Since its discovery, the hydroboration reaction has become one of the most valuable synthetic techniques in organic chemistry. Although conventional hydroboration agents such as H_3B·X (X = THF, SMe_2, BH_3), thexylborane, and 9-BBN react readily with unsaturated organic fragments, reactivity of other boranes can be quite sluggish.[2]

That transition metals could accelerate such reactions was initially reported for catalyzed hydroborations of alkenes and alkynes using polyhedral boranes.[3,4] Männig and Nöth[5] then demonstrated that [RhCl(PPh_3)$_3$] (**1**) catalyzed hydroboration of alkenes with catecholborane, HBcat (cat = 1,2-$O_2C_6H_4$), under mild conditions and with chemoselectivity differing from that of the uncatalyzed reaction[6] (Scheme I). A catalytic cycle has been proposed[5] which resembles that suggested previously[4] for rhodium-catalyzed addition of carborane B—H bonds to the C=C unit in acrylate esters. Catalyzed hydroboration is believed to proceed via initial oxidative addition of HBcat to the metal center, affording known five-coordinate complex [RhHCl(Bcat)(PPh_3)$_2$] (**2**),[5,7] with subsequent insertion of alkene into the Rh-H bond and reductive elimination of the B-C bond. We reported recently the synthesis and molecular structure of unsaturated hydrido-boryl complex [RhHCl(Bcat)(PPr^i_3)$_2$] (**3**), the triisopropylphosphine analogue of **2**.[8] Oxidative addition of B-H bonds of HBcat, 9-BBN, and thexylborane to phosphinoiridium(I) complexes has also been reported.[9,10]

Since Nöth's original findings,[5] much attention has been focused on exploiting transition metal-catalyzed hydroborations for applications in organic synthesis.[11] Catalyzed hydroborations often give complementary regio-[12] and diastereoselectivity[12a,13] to those observed using conventional hydroboration agents such as 9-BBN. In particular, a combination of high Markovnikov selectivity and

Scheme I



efficient chirality transfer affords chiral alcohols via addition of HBcat to vinylarenes at low temperatures catalyzed by [Rh(diene)(P_2)]$^+$A$^-$ (diene = 1,5-cyclooctadiene or 2,5-norbornadiene; P_2 = chiral bis(phosphine); A$^-$ = noncoordinating anion).[14-17]

† Dedicated to the memory of Dr. Theodore A. Annan, a respected colleague and friend. He will be sorely missed.

‡ University of Waterloo.

§ E. I. du Pont de Nemours and Co.

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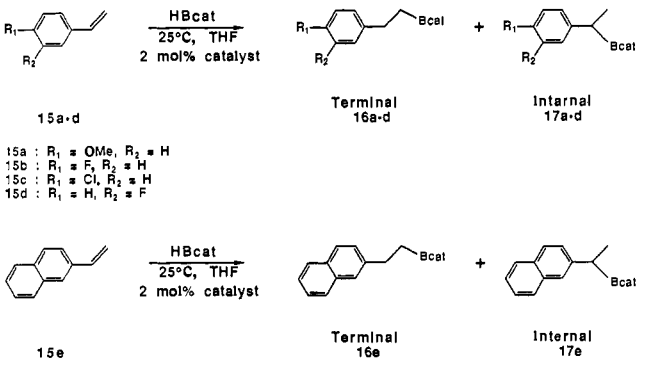
0002-7863/92/1514-8863$03.00/0

Table I. Hydroboration of Vinylarenes **15a–e**[a]

catalyst	substrate	% terminal[b] **16a–e**	% internal[b] **17a–e**
1[c]	**15a–e**		>99
9	**15a–e**		>99
10	**15a**		>99
11[d]	**15a**		>99
12	**15a**		>99
7[d]	**15a**	5	95
6	**15a**	10	90
14[e]	**15a**	15	85
5	**15a**	20	80
8	**15a**	45	55
13[e]	**15a**	55	45
4	**15a**	95	5

[a] All reactions were carried out in THF at room temperature in the presence of 2 mol % catalyst. Alkene/catecholborane/catalyst = 1.0/1.1/0.02. [b] Determined by ^{13}C and ^{1}H NMR. [c] Ca. 5% of hydrogenation observed for all substrates. [d] Reactions also carried out in CD_2Cl_2. [e] Ca. 30% of hydrogenation product observed.

Scheme II



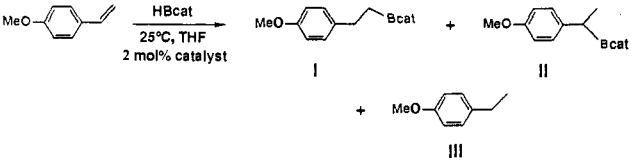
With aliphatic 1-alkenes, however, cationic catalyst precursors gave similar selectivities[12a,16b] to those of the 80 °C uncatalyzed addition of HBcat.[6] Furthermore, while significantly higher regioselectivities (99% at 25 °C) were observed using **1** as catalyst, recent studies have shown that product distributions are dependent on catalyst purity[16,18] and competing alkene hydrogenation.[19]

We have used multinuclear NMR spectroscopy to examine primary products from catalyzed hydroborations of alkenes using a variety of transition metal phosphine complexes. We report herein on a series of new hydroboration catalyst precursors which exhibit both high activity and excellent regioselectivity for a wide range of alkenes.

Results

Rhodium-Catalyzed Hydroboration of Vinylarenes. Our initial work focused on catalyzed hydroboration of 4-vinylanisole (**15a**), a substrate which reacts otherwise with HBcat only at elevated temperatures (ca. 100 °C), yielding predominantly terminal alkylboronate ester **16a**, (**16a**:**17a** = 90:10).[2] Stereochemical assignment of internal and terminal boronate esters is based upon

Scheme III



Catalyst	I	II	III
[Rh(η^6-catBcat)(DPPE)]	·	>99	·
[Rh(η^6-catBcat)(DiPPE)]	·	>99	·
[Rh(η^6-PhBPh$_3$)(DPPE)]	11	60	29
[Rh(η^6-PhBPh$_3$)(DiPPE)]	39	31	30

Table II. Hydroboration of (*E*)-1-Phenylpropene (**18**)[a]

catalyst	% terminal[b]	% internal[b]
1[c]	30	70
7[d,e]		>99
11[d]		>99
9		>99
10		>99
12		>99

[a] All reactions were carried out in THF at room temperature in the presence of 2 mol % catalyst. Alkene/catecholborane/catalyst = 1.0/1.1/0.02. [b] Determined by ^{13}C and ^{1}H NMR. [c] Ca. 5% of *n*-propylbenzene formed by hydrogenation. [d] Reactions also carried out in CD_2Cl_2. [e] Ca. 25% conversion after 96 h.

^{1}H and ^{13}C NMR spectroscopic data. Particularly diagnostic was the proton-coupled ^{13}C NMR spectrum, wherein the doublet B–C–H resonance of the internal boronate ester is broadened severely due to coupling to the quadrupolar ^{11}B nucleus. In addition, reactions were monitored by ^{11}B NMR spectroscopy[20] to determine efficiency of addition of HBcat to the alkene. Furthermore, multinuclear NMR spectroscopic investigations reveal when one or more hydroboration products is formed (cf. addition of BH_3, see later) in reaction mixtures which yield a single alcohol after oxidative workup.[19a]

Results summarized in Table I show regioselectivities (forming **16a** or **17a**) are strongly dependent on the nature of phosphine ligands coordinated to rhodium. Hydroboration of **15a** with HBcat in the presence of 2 mol % [RhCl(N_2)(PPr^i_3)$_2$] (**4**) proceeded with selectivity that directly parallels that found in the conventional uncatalyzed reaction.

Using [Rh(μ-Cl)(DiPPE)]$_2$ (**5**) (DiPPE = 1,2-bis(diisopropylphosphino)ethane), [RhCl{P(O-*o*-tol)$_3$}$_3$] (**6**), or [Rh(COD)(DiPPE)]OTf (**7**) (COD = 1,5-cyclooctadiene) as catalyst precursor gave moderate selectivity in favor of internal boronate ester. This is of interest as no new Rh-containing products were observed when **5–7** were treated with stoichiometric or excess amounts of catecholborane in the absence of substrate. Degradation of catecholborane was eventually observed, however, resulting in formation of B_2cat_3[21b] and highly reactive hydroborating reagent H_3B·THF, via boron substituent redistribution.[22]

Hydroboration of vinylarenes **15a–e** with HBcat in the presence of **1** proceeded with high regioselectivity (>99:1) forming benzyl boronate esters **17a–e** (Scheme II).[23] Although no CH_2B groups

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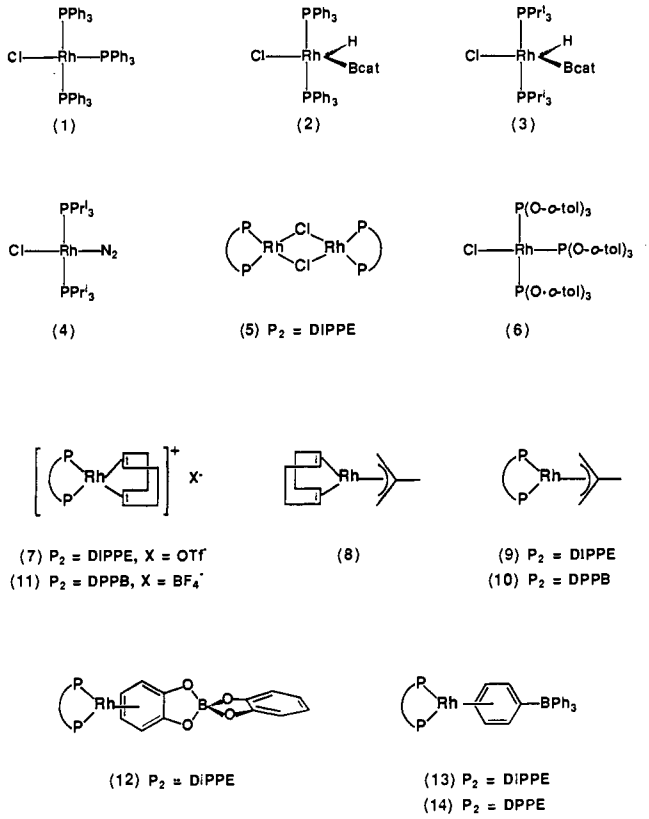
Chart I



were detected by ^1H or ^{13}C NMR spectroscopy, alkene hydrogenation was observed to some extent (ca. 5%) with all substrates.

Likewise, excellent activity and Markovnikov selectivities were also found for catalyzed hydroboration of substrates **15a–e** using [Rh(η^3-2-Me-allyl)(DiPPE)] (**9**)[24] as catalyst precursor. Hydroborations with the rhodium catalyst generated in situ by treating [Rh(η^3-2-Me-allyl)(COD)] (**8**) with DiPPE in THF were comparable to those using preformed catalyst **9**. Similar activities and regioselectivites were obtained for reactions run in toluene or at low temperatures (−30 °C). High chemical yields and Markovnikov selectivities were also observed for reactions employing phenylphosphine analogue [Rh(η^3-2-Me-allyl)(DPPB)] (**10**) (DPPB = 1,4-bis(diphenylphosphino)butane). A previous report[16b] on hydroboration of 2-vinylnaphthalene (**15e**) using [Rh(COD)(DPPB)]BF_4 (**11**) indicated surprisingly low regioselectivity (65:35) in favor of internal boronate ester **17e**. However, we found hydroborations of vinylarenes **15a–e** using **11** *all* proceeded with complete regiocontrol (>99%) in favor of internal boronate esters.

We have shown previously[8] that addition of excess catecholborane to **9** results in quantitative formation of zwitterionic species [Rh(η^6-catBcat)(DiPPE)] (**12**). Hydroborations carried out with isolated zwitterion **12**[8,21c] were comparable to those catalyzed by **9**, giving internal boronate esters exclusively. Surprisingly, hydroborations catalyzed by either of the analogous zwitterions [Rh(η^6-$PhBPh_3$)(DiPPE)] (**13**) or [Rh(η^6-$PhBPh_3$)(DPPE)] (**14**) gave a mixture of internal and terminal boronate esters, as well as considerable amounts of hydrogenation product (Scheme III).

Catalyzed hydroboration of β-substituted styrenes with **9** at 25 °C gave α-boronate esters in quantitative yield (Table II). Relative to styrenes **15a–e**, sterically hindered vinylarenes (*E*)-1-phenylpropene (**18**) and indene (**21**) required somewhat longer reaction times to reach completion ($t_{1/2}$ = ca. 1 h for 2 mol % Rh). Activities for hydroborations of **18** carried out in the presence of **9** were comparable to those using cationic catalyst precursor **11** and both reactions proceeded with complete regiocontrol.[16b]

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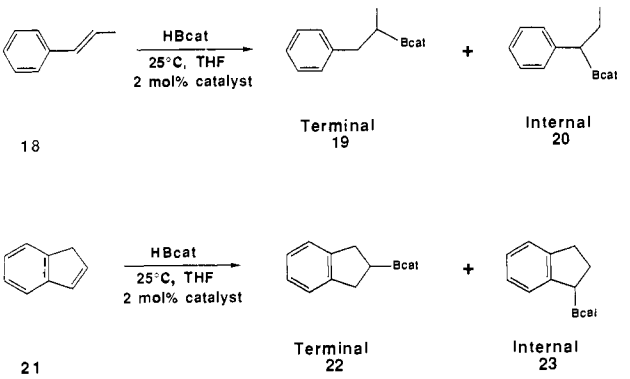
Scheme IV



Scheme V

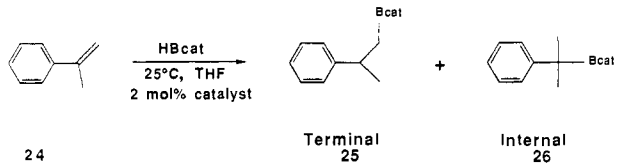


Table III. Hydroboration of 2-Phenylpropene (**24**) with [Rh(η^3-2-Me-allyl)P_2][a]

phosphine,[b] P_2 =	time, h	% terminal[c]	% internal[c]	% isopropylbenzene[c]	% BH_3 products[d]
DiPPE	2		85		15
DCPE	6		70		30
DiPPP[e]	24	44	11	5	40
DiPPB[e]	12	44	1	5	50
DPPE	0.5	30	70		
DPPP	0.5	20	80		
DPPB	0.5	5	95		

[a] All reactions were carried out in THF at room temperature in the presence of 2 mol % catalyst. Alkene/catecholborane/catalyst = 1.0/1.2/0.02. [b] DCPE = 1,2-bis(dicyclohexylphosphino)ethane; DiPPP = 1,3-bis(diisopropylphosphino)propane; DiPPB = 1,4-bis(diisopropylphosphino)butane; DPPE = 1,2-bis(diphenylphosphino)ethane; DPPP = 1,3-bis(diphenylphosphino)propane. [c] Determined by ^{13}C and ^1H NMR. [d] Products arising from addition of BH_3 formed by degradation of HBcat. [e] Vinylboronate ester formation also observed in small quantities (<1%).[19]

Alkene hydrogenation was also negligible in hydroboration of styrenes **15a–e**, **18**, and **21** catalyzed by both **9** and **11**.

Hydroboration of 2-phenylpropene (**24**) using **9** gave excellent regioselectivity for internal boronate ester **26** (Scheme V). With this substrate, however, we observed formation of *alkylboranes* derived from addition of BH_3 to **24**. Hydroboration of **24** with H_3B·THF favors the terminal alkylborane,[2] and upon oxidation, therefore, the ratio of the two alcohols would not be representative of the ratio of boronate ester primary products. While analogous reactions of **24** using **1**[19b] or **11**[16] do not give BH_3-derived products, the ratio of **25**:**26** using **11** is only 30:70.

In order to maximize formation of internal boronate ester **26**, we examined the effect of varying phosphine ligands in [Rh(η^3-2-Me-allyl)(P_2)] on catalyzed hydroborations of 2-phenylpropene. In situ catalyst generation via addition of various phosphines to **8** allowed for fine tuning of steric and/or electronic properties of the catalyst. Increasing the number of methylenes (*n*) in the chelate backbone clearly has a dramatic effect on catalyst activity and selectivity (Table III). For bulky phosphines DiPPP and DiPPB, rates decrease and the amounts of BH_3-derived products increase with *n*. The last three entries in Table III indicate the superiority of arylphosphines over corresponding bulky alkylphosphines for hydroboration of 2-phenylpropene. No BH_3-derived products were observed using arylphosphine derivatives, and [Rh(η^3-2-Me-allyl)(DPPB)] (**10**) gave the highest yield of internal boronate ester **26** (95%) for any catalyst precursor.[16b,19b]

Scheme VI

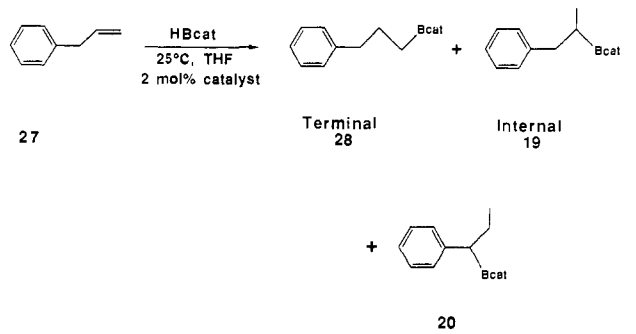


Table IV. Hydroboration of 2,3-Dimethylbut-2-ene (32)[a]

catalyst	% hydroboration product 33[b]	time, h
1		100
7[c]		100
11[c]	82	100
9	>99	80
10	>99	24

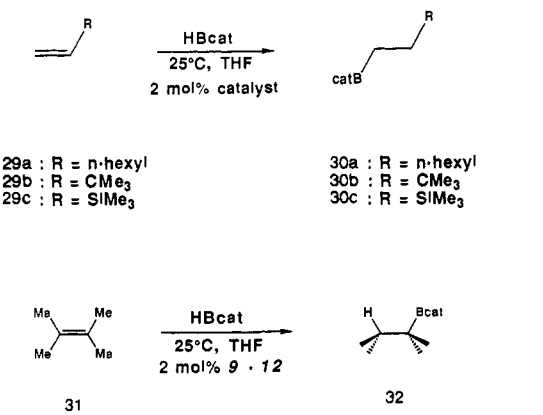
[a] All reactions were carried out in THF at room temperature in the presence of 2 mol % catalyst. Alkene/catecholborane/catalyst = 1.0/1.5/0.02. [b] Determined by ^{13}C and ^{1}H NMR. [c] Reactions also carried out in CD_2Cl_2.

In general, high selectivities forming secondary boronate esters were observed in rhodium-catalyzed hydroboration of styrenes.[12b,14-18,25] To date, Markovnikov selectivities have been found only for alkenes in which aromatic groups are attached directly to the double bond.[16] To illustrate this point, we examined catalytic hydroboration of 1-phenylprop-2-ene (**27**), where the aromatic group is now β to the alkene moiety. While this reaction indeed gave moderate regioselectivity in favor of terminal boronate ester **28**, significant amounts of **19** and **20** were also observed (**28**:**19**:**20** = 65:33:2). Alkylboronate ester **20** arises from isomerization of **27** to (*E*)-1-phenylpropene (**18**). Similar product distributions were also observed for hydroborations of **27** using **11** (**28**:**19**:**20** = 75:16:9) and **1** (**28**:**19**:**20** = 70:9:21).

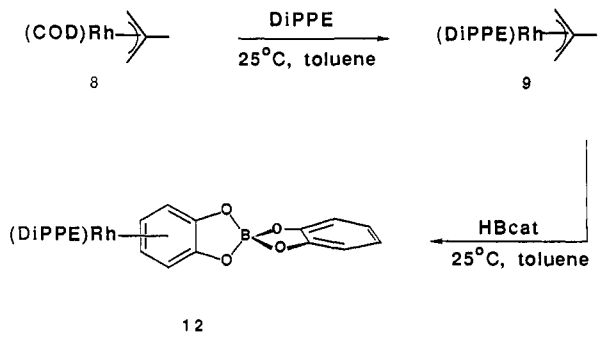
Rhodium-Catalyzed Hydroboration of Aliphatic Alkenes. Hydroborations of 1-octene (**29a**) with **1** and **9** proceeded with high selectivity (at 25 °C for 0.5 h) forming terminal boronate ester **30a** in nearly quantitative yield. The analogous reaction with **11**, however, gave ca. 6% of the internal product derived from alkene isomerization.[12a,16b] We also observed high conversion and selectivities (>99%), using **1**, **9**, and **11**, for catalyzed hydroborations of bulky alkenes 3,3-dimethylbut-1-ene (**29b**) and vinyltrimethylsilane (**29c**). Alkene hydrogenation was negligible for these substrates, and activities were all comparable. More remarkable, however, is that 2,3-dimethylbut-2-ene (**31**) was hydroborated catalytically at 25 °C using **9** and **11**. To our knowledge, this is the first example of catalyzed hydroboration of a tetrasubstituted alkene. Although the reaction was sluggish ($t_{1/2}$ = ca. 40 h for 2 mol % Rh) for bulky alkylphosphine complex **9**, formation of tertiary boronate ester **32** was quantitative. Much faster rates were observed in hydroborations of **31** employing arylphosphine analogue **10** ($t_{1/2}$ = ca. 12 h for 2 mol % Rh). Although cationic complex **11** also catalyzed hydroboration of this sterically demanding alkene ($t_{1/2}$ = ca. 50 h for 2 mol % Rh), yields were ultimately limited by catalyst decomposition. In the later stages of the reaction, alkylboranes were formed by addition of BH_3 to **31** and its isomer 2,3-dimethylbut-1-ene. Attempts to catalyze the hydroboration of **31** with **1** failed (Table IV).

Fate of the Catalyst Precursor. Efficiency of catalyzed hydroborations was also investigated by ^{11}B, ^{31}P, and in some cases ^{19}F NMR spectroscopy to determine the fate of catalyst precursors. As reported in detail elsewhere,[19a] hydroboration reactions employing $[RhCl(PPh_3)_3]$ (**1**) invariably lead to formation of boryl complex $[RhHCl(Bcat)(PPh_3)_2]$ (**2**) and dihydride $[RhH_2Cl(PPh_3)_3]$,[26] along with varying amounts of HBcat degradation products. Hydroborations using cationic diene complexes, $[Rh(COD)(DPPB)]^+A^-$ (A = BF_4, SbF_6), were much more complicated as both anion and diene ligand are susceptible to attack by boron species in solution; the nature of products formed depended on alkene substrate. While Rh-containing products were not all identified, Rh metal formation was eventually observed for demanding substrates such as 2,3-dimethylbut-2-ene (**31**) (see Experimental Section). For most alkene hydroborations using **9**, on the other hand, only **12** was present *in observable quantities* at any time during or after completion of catalysis. Only for hydroboration of 2-phenylpropene (**24**) did we observe additional Rh-containing products using **9**. In this case, we observed formation of Rh(III) byproducts which arise presumably from reactions of **12** with BH-containing organoboranes,[27] derived from addition of BH_3 to **24**. These byproducts were not observed with arylphosphine analog **10**.

Scheme VII



Scheme VIII



Discussion

Addition of 1 equiv of chelating bidentate phosphine DiPPE to **8** affords **9** in nearly quantitative yield.[24] Complex **9** is inherently different from all catalyst precursors previously employed for hydroboration of alkenes due to increased steric bulk and basicity of alkylphosphine ligands. We have shown[8] addition of excess catecholborane to **9** results in quantitative formation of zwitterionic species **12**. Further details of the conversion of **9** to **12**, along with the molecular structure of novel dinuclear intermediate $[Rh(DiPPE)(\mu\text{-}H)_2(\mu\text{-}Bcat)RhH(DiPPE)]$, will be reported elsewhere.[21c]

Recently, two groups[16,23,25] reported that product distributions from catalyzed hydroborations are strongly dependent upon concentration and nature of phosphine ligands coordinated to rhodium. For hydroborations of styrenes, high anti-Markovnikov selectivities were observed in reactions catalyzed by $[Rh(COD)_2]BF_4$.[23] Addition of 2 equiv of PPh_3 changed the ratio of internal to terminal alcohols to 59:41. Further addition of PPh_3 (4 equivs) increased selectivity toward internal boronate ester to

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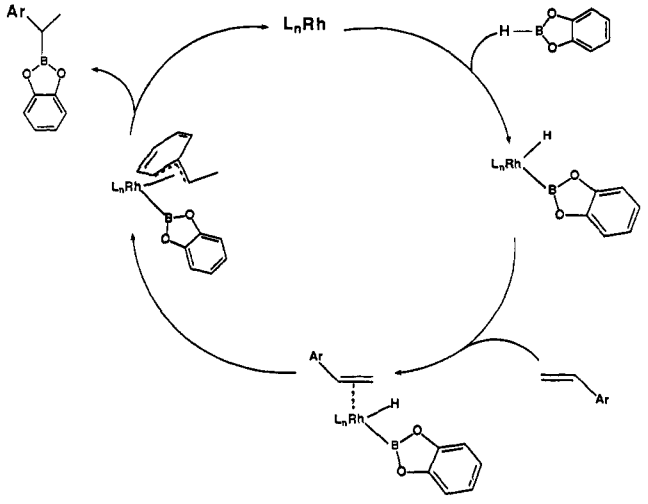
Scheme IX



98:2. Likewise, hydroboration of styrenes catalyzed by **1** proceeds with excellent selectivity (>99%) affording corresponding secondary boronate esters. Catalyst purity is essential for high selectivities[18] as hydroborations carried out in the presence of oxidized **1** favor formation of terminal boronate esters.

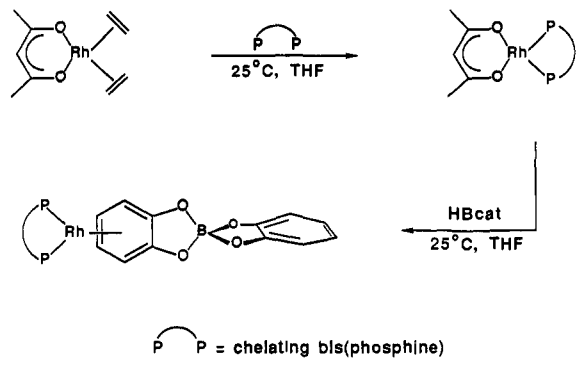
A modified catalytic pathway has been proposed recently[16] to explain unique Markovnikov selectivities observed in rhodium-catalyzed hydroborations of styrenes. This mechanism invokes an η^3-benzylrhodium intermediate as shown in Scheme IX. Reductive elimination from this species should produce the secondary boronate ester exclusively. Consistent with this hypothesis, recent results[21c,27] in our laboratories demonstrated that in stoichiometric reactions of η^3-allyl rhodium complexes with hydroborating reagents the boron unit always becomes attached to a terminal carbon of the allyl moiety. Of particular relevance to this work is the reaction of 9-BBN with **9** to give [Rh(HBR$_2$CH$_2$CMe=CH$_2$)(DiPPE)].[21c]

In this study we found a wide range of selectivities for the hydroboration of 4-vinylanisole (**15a**) with HBcat as the catalyst was varied (Table I). While poor selectivity was obtained with phosphine ligand-free [Rh(η^3-2-Me-allyl)(COD)] (**8**), addition of chelating phosphines (**9**, **10**) gave essentially quantitative formation of internal boronate ester **17a**. Using [RhCl(N$_2$)(PPr$^i_3$)$_2$] (**4**), however, we observed preferential formation of terminal product **16a**. This anti-Markovnikov selectivity arises presumably from increased steric bulk of monodentate PPr$^i_3$ ligands (compared with PPh$_3$ in **1**) which could inhibit formation of the η^3-benzylrhodium intermediate, disfavoring this catalytic pathway. The competing conventional catalytic pathway could then take precedence, resulting in predominant formation of terminal boronate esters.

Alternative mechanisms for catalyzed hydroborations are also conceivable. That complexes **5–7** catalyze hydroborations of styrenes, but fail to react stoichiometrically with HBcat, suggests that coordination of alkene may precede BH oxidative addition in the catalytic cycle.

Efficiency of catalyst precursors also depends on alkene substrate. For vinylarenes, **1**, **9**, and cationic **11** all exhibited excellent activity and selectivity, while cationic DiPPE analog **7** gave 5% terminal product in hydroboration of **15a**. With sterically demanding alkenes, activity and selectivity of hydroborations using **1** decreased dramatically. Although **11** is an effective catalyst for substituted vinylarenes, hydroborations of aliphatic alkenes gave isomerization and BH$_3$-derived products arising from catalyst degradation. Degradation of **9** was unique to hydroborations of 2-phenylpropene and was not observed to any extent for arylphosphine analog **10**; in general only zwitterionic **12** and its arylphosphine analog were observed in solution upon completion of catalysis. This is in contrast to catalytic reactions employing **1**[19a] and **11** (see Experimental Section) wherein several Rh species

Scheme X



were present in solution. Indeed, isolated **12** gave catalytic results identical with those found for **9**, and it seems likely that **12** is the "immediate catalyst precursor".

In complex **12**, the [B(cat)$_2$]$^-$ anion is π-bound to rhodium in an η^6-fashion through one of the arene rings, similar to that in zwitterionic [BPh$_4$]$^-$ complexes **13** and **14**. A single crystal X-ray diffraction study[28] on **14** has shown that the coordinated phenyl ring assumes a distorted boat conformation in which two carbon atoms are closer to the metal center than the remaining four carbons. This distortion in the phenyl ring has been attributed to formation of partially localized covalent bonds between rhodium and two phenyl carbon atoms. In contrast, we observed a modest degree of slippage[29] of the Rh atom away from the arene ring centroid in the molecular structure of **12**. It would appear that further ring slippage toward η^4- or η^2-coordination of the [B(cat)$_2$]$^-$ ligand is facile, providing readily available coordination sites for substrate activation. Dissociation of a labile ligand, such as PPh$_3$, usually provides additional vacant coordination sites required at the metal center in homogeneous catalysis.[30] Similar activity and selectivity using **9** in THF and in toluene suggests that the [B(cat)$_2$]$^-$ anion may not dissociate fully from Rh during catalysis.

Catalyst solutions were reused with fresh substrate with no appreciable decrease in activity and/or selectivity; 600 turnovers were observed under unoptimized reaction conditions. Although **8** is both air and thermally sensitive, and **9** is air sensitive, isolated pure **12** appears to be reasonably air stable in crystalline form. We have observed recently that [Rh(η^6-catBcat)(P$_2$)] zwitterions are also obtained in high yields from reactions of HBcat with [Rh(acac)(P$_2$)] (acac = acetylacetonate).[31] The stable [Rh(acac)(P$_2$)] precursors are prepared readily by addition of phosphine ligands to commercially available [Rh(acac)(η-C$_2$H$_4$)$_2$] (Scheme X). Preliminary results of hydroborations using [Rh(acac)(P$_2$)] precursors were identical with those found for either **9** or **12**.

Conclusions

Allyl complex **9** is a very active, highly selective catalyst precursor for addition of HBcat to a wide range of alkenes. Unlike catalysts reported previously, **9** gives excellent selectivity for both aryl- and aliphatic alkenes and accommodates sterically demanding alkenes without hydrogenation or isomerization. The efficiency of **9** is attributed to the lability of the π-bonded [B(cat)$_2$]$^-$ anion in the proposed zwitterionic catalyst resting state. Finally, addition of phosphines to [Rh(η^3-2-Me-allyl)(COD)] or [Rh(acac)(C$_2$H$_4$)$_2$] allows one to "fine tune" the catalyst to match the substrate. Investigations using chiral bidentate phosphines for asymmetric hydroborations of prochiral alkenes are in progress.

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Experimental Section

General Procedures. NMR spectra were recorded on General Electric QM-300 (^{1}H at 300 MHz, ^{13}C at 75.4 MHz, ^{31}P at 121 MHz), Nicolet NMC-300 (^{11}B at 96 MHz), and Nicolet NMC-200 (^{19}F at 188 MHz) spectrometers in THF-d_8 (tetrahydrofuran) unless stated otherwise. ^{1}H NMR chemical shifts are reported in ppm relative to external TMS and were referenced to residual protons in THF-d_8; coupling constants are in hertz. Multiplicities are reported as (s) singlet, (d) doublet, (t) triplet, (q) quartet, (sext) sextet, (m) multiplet, (br) broad, and (ov) overlapping. ^{11}B, ^{19}F, and ^{31}P chemical shifts are reported in ppm relative to external standards $F_3B{\cdot}OEt_2$, CCl_3F, and 85% H_3PO_4, respectively. ^{13}C chemical shifts are reported in ppm relative to external TMS using THF-d_8 (25.3) as an internal standard. Carbon multiplicities are listed as (C) quaternary, (CH) methine, (CH_2) methylene, and (CH_3) methyl. THF and toluene were freshly distilled from sodium benzophenone ketyl. Catecholborane (Aldrich Chemical Co.) was distilled under reduced pressure. Alkenes were purchased from commercial suppliers and used as received. DiPPE,[32] DiPPP,[33] and DiPPB[33] were prepared via literature methods. Reagent purity was ascertained by ^{1}H NMR spectroscopy. Wilkinson's catalyst,[34] $[Rh(\mu\text{-}Cl)(COD)]_2$,[35] $[Rh(COD)(DPPB)]BF_4$,[36] $[Rh(\eta^3\text{-}2\text{-}Me\text{-}allyl)(COD)]$,[24] and $[RhCl(N_2)(PPr^i_3)_2]$[37] were prepared by established methods. $[Rh(\eta^6\text{-}PhBPh_3)(DiPPE)]$[28] (**13**) was prepared by an established method replacing DPPE with DiPPE. Selected NMR spectroscopic data for **13** (in CD_2Cl_2): $^{31}P\{^1H\}$ 74.0 (d, J_{PRh} = 206 Hz); $^{11}B\{^1H\}$ −7.8 (s); ^1H δ 0.94, 0.97 (d d, $^3J_{HH}$ = 7 Hz, $^3J_{HP}$ = 13 Hz, 12 H, CH_3), 1.44 (br d, $^2J_{HP}$ = 12 Hz, 4 H, PCH_2CH_2P), 1.59 (ov m, 4 H, CH), 6.08 (ov d d, $^2J_{HH}$ = 6 Hz, 2 H, Ph), 6.53 (t, $^2J_{HH}$ = 6 Hz, 1 H, Ph), 6.66 (ov d d, $^2J_{HH}$ = 6 Hz, 2 H, Ph), 6.97 (t, $^2J_{HH}$ = 7 Hz, 3 H, Ph), 7.06 (ov d d, $^2J_{HH}$ = 7 Hz, 6 H, Ph), 7.18 (br ov d d, $^2J_{HH}$ = 7 Hz, 6 H, Ph).

Preparation of $[Rh(\mu\text{-}Cl)(DiPPE)]_2$ (5). A solution of DiPPE (262 mg, 1.0 mmol) in 25 mL of hexane was added dropwise to a suspension of $[Rh(\mu\text{-}Cl)(COE)_2]_2$[38] (359 mg, 0.5 mmol, COE = *cis*-cyclooctene) in 25 mL of hexane. After being stirred for 1 h, the solution was concentrated in vacuo to 10 mL and cooled at −30 °C for 48 h. The resulting yellow crystals were filtered, washed with cold pentane, and dried in vacuo; yield 277 mg (69%). Complex **5** was characterized spectroscopically by ^{1}H and ^{31}P NMR. Selected NMR spectroscopic data (in THF-d_8): $^{31}P\{^1H\}$ 103.6 (d, J_{PRh} = 200 Hz); ^1H δ 1.10, 1.35 (d d, $^3J_{HH}$ = 7 Hz, $^3J_{HP}$ = 13 Hz, 12 H, CH_3), 1.32 (br d, $^2J_{HP}$ = 12 Hz, 4 H, PCH_2CH_2P), 2.05 (ov m, 4 H, CH).

Preparation of $[RhCl\{P(O\text{-}o\text{-}tol)_3\}_3]$ (6). A solution of $P(O\text{-}o\text{-}tol)_3$ (352 mg, 1.0 mmol) in 10 mL of toluene was added dropwise to a suspension of $[Rh(\mu\text{-}Cl)(COE)_2]_2$ (120 mg, 0.17 mmol) in 10 mL of toluene. After being stirred for 1 h, the solution was concentrated in vacuo to 5 mL and cooled at −30 °C for 48 h. The resulting yellow crystals were filtered, washed with cold pentane, and dried in vacuo; yield 336 mg (84%). Complex **6** was characterized spectroscopically by ^{1}H and ^{31}P NMR. Selected NMR spectroscopic data (in THF-d_8): $^{31}P\{^1H\}$ 111.0 (d d, J_{PRh} = 225 Hz, $^2J_{PP}$ = 53 Hz), 119.5 (d t, J_{PRh} = 286 Hz, $^2J_{PP}$ = 53 Hz); ^1H δ 1.82 (s, 6 H, CH_3), 1.90 (s, 3 H, CH_3), 6.87–7.09 (ov m, 12 H, Ph).

Preparation of [Rh(COD)(DiPPE)]OTf (7). A solution of DiPPE (26 mg, 0.1 mmol) in 5 mL of toluene was added dropwise to a suspension of $[Rh(COD)_2]OTf$[39] (47 mg, 0.1 mmol) in 5 mL of toluene. After being stirred for 1 h, the solvent was removed in vacuo and the yellow residue was triturated with Et_2O, filtered, and dried in vacuo; yield 58 mg (93%). Complex **7** was characterized spectroscopically by ^{1}H and ^{31}P NMR. Selected NMR spectroscopic data (in CD_2Cl_2): $^{31}P\{^1H\}$ 76.9 (d, J_{PRh} = 147 Hz); ^1H δ 1.22, 1.30 (d d, $^3J_{HH}$ = 7 Hz, $^3J_{HP}$ = 14 Hz, 12 H, CH_3), 1.83 (br d, $^2J_{HP}$ = 14 Hz, 4 H, PCH_2CH_2P), 2.33 (ov m, 12 H, CH and COD), 5.43 (br s, 4 H, COD).

General Procedure for the Catalyzed Hydroboration of Alkenes. All reactions were carried out under an atmosphere of dry nitrogen using a continuous purge Vacuum Atmospheres glovebox. Catecholborane (250 mg, 2.1 mmol), in 1 mL of THF-d_8, was added dropwise to a mixture of alkene (2.0 mmol) and catalyst (0.04 mmol) in 1 mL of THF-d_8. Identical results were obtained if alkene was added to a mixture of catecholborane and catalyst. The resulting solutions were stirred for 30 min and then analyzed by high-field ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy. Samples were sufficiently concentrated that small quantities of minor products, if present in solution, could be detected by NMR spectroscopy. Oxidative workup of alkylboronate esters formed in catalyzed hydroboration reactions afforded the corresponding alcohols. In several experiments, alcohol product distributions were confirmed by GC or HPLC.

Fate of the Catalyst Precursors during Catalysis. (i) Hydroboration reactions using **1** are complicated by formation of several phosphinorhodium(I) complexes and HBcat degradation products as reported in detail elsewhere.[19a] (ii) Selected NMR spectroscopic data for catalytic hydroborations of vinylarenes, excluding 2-phenylpropene, and aliphatic alkenes using **9** (in toluene-d_8): $^{31}P\{^1H\}$ 106.9 (d, J_{PRh} = 209 Hz, **12**); $^{11}B\{^1H\}$ 15.1 (s, **12**).[8] Hydroborations of 2-phenylpropene were complicated by formation of BH_3 arising from metal-mediated degradation of HBcat. Selected NMR spectroscopic data (in THF-d_8): $^{31}P\{^1H\}$ 105.1 (d, J_{PRh} = 168 Hz), 104.7 (d, J_{PRh} = 209 Hz, **12**), 80.2 (br d, J_{PRh} = 152 Hz), 75.4 (d, J_{PRh} = 112 Hz), 73.2 (d, J_{PRh} = 129 Hz); $^{11}B\{^1H\}$ 86.5 (br, BH_3-derived product), 35.4 (br, **26**), 18.4 (br, B_2cat_3), 14.9 (s, **12**). Hydroborations of 2-phenylpropene carried out in the presence of analogous arylphosphine catalyst precursor **10** gave corresponding zwitterion $[Rh(\eta^6\text{-}catBcat)(DPPB)]$ as the only phosphinorhodium complex in solution (at detectable levels). Selected NMR spectroscopic data (in THF-d_8): $^{31}P\{^1H\}$ 43.7 (d, J_{PRh} = 206 Hz); $^{11}B\{^1H\}$ 35.3 (br, **26**), 15.0 (s, $[B(cat)_2]^-$). (iii) Selected NMR spectroscopic data for catalytic hydroborations of 4-vinylanisole **15a** using **11** (in CD_2Cl_2): $^{31}P\{^1H\}$ 24.2 (d, J_{PRh} = 143 Hz, **11**), 40.5 (d, J_{PRh} = 198 Hz, major); ^{19}F −128.3 (s, minor), −144.8 (br), −149.2 (br), −156.4 (s, **11**); $^{11}B\{^1H\}$ 34.6 (br, **17a**), 22.4 (br, B_2cat_3), 7.4 (br, minor), −0.5 (s, minor, **11**). While catalytic hydroborations of (*E*)-1-phenylpropene (**18**) using **11** afforded several new phosphinorhodium complexes, particularly interesting was the notable absence of any RhH-containing species. Selected NMR spectroscopic data (in CD_2Cl_2): $^{31}P\{^1H\}$ 24.2 (d, J_{PRh} = 143 Hz, **11**), 33.3 (br), 39.6 (d, J_{PRh} = 197 Hz, minor), 40.5 (d, J_{PRh} = 198 Hz, major); ^{19}F −144.3 (br), −150.1 (br, major), −156.5 (s, **11**) −158.9 (br s); $^{11}B\{^1H\}$ 34.6 (br, **20**), 22.2 (br, B_2cat_3, minor), 6.5 (br, minor), −0.5 (s, **11**). Hydroborations of bulky 2,3-dimethylbut-2-ene (**31**) using **11** were complex, and eventually degradation of catalyst and HBcat (into BH_3 and B_2cat_3) was observed. Selected NMR spectroscopic data (in CD_2Cl_2): $^{31}P\{^1H\}$ −3.0 (br), 15.7 (br), 18.2 (br), 28.0 (d, J_{PRh} = 110 Hz), 28.2 (br), 36.0 (br), 46.9 (br), 48.1 (d, J_{PRh} = 156 Hz); ^{19}F −38.6 (d, J = 137 Hz), −144.4 (br, minor), −149.1 (s); $^{11}B\{^1H\}$ 79.8 (br, minor, BH_3-derived product), 59.3 (br, minor, BH_3-derived product), 35.5 (br, **32**), 28.7 (s, minor), 22.5 (br, B_2cat_3). Stoichiometric reactions of **11** with HBcat (3 equiv) were extremely complex as HBcat reacted with the $[BF_4]^-$ anion. Selected NMR spectroscopic data (in CD_2Cl_2): $^{31}P\{^1H\}$ many broad peaks and overlapping doublets due to phosphinorhodium complexes observed between 0 and 50 ppm; ^{19}F −144.5 (br), −148.2 (br), −149.2 (br), −156.3 (s, **11**); $^{11}B\{^1H\}$ 35.3 (br), 22.8 (br, B_2cat_3), 3.5 (br), −0.3 (s, **11**), −40.2 (br, minor, $H_3B{\cdot}DPPB$). Degradation products were also observed with the $[SbF_6]^-$ analog of **11**. Catalyst activities using this $[SbF_6]^-$ salt were reduced greatly for all substrates (for **15a**; $t_{1/2}$ = ca. 12 h for 2 mol % Rh), and in some cases (i.e. 2-phenylpropene), regioselectivities were also reduced.

Catalytic Hydroboration of 15a: (a) Synthesis of 16a. ^{1}H NMR: δ 1.55, 2.90 (t, J = 8 Hz, 2 H, CH_2), 3.65 (s, 3 H, OCH_3), 6.73–7.17 (ov m, 8 H, Ph and cat). ^{13}C NMR: 13.5 (br, B–CH_2), 29.6 (CH_2), 55.3 (OCH_3), 112.9 (CH), 114.5 (CH), 123.2 (CH), 129.4 (CH), 136.5 (C), 149.3 (C), 159.0 (C). $^{11}B\{^1H\}$ NMR: 35.5 (br).

(b) Synthesis of 17a. ^{1}H NMR: δ 1.52 (d, J = 8 Hz, 3 H, CH_3), 2.88 (q, J = 8 Hz, 1 H, CH), 3.67 (s, 3 H, OCH_3), 6.75–7.14 (ov m, 8 H, Ph and cat). ^{13}C NMR: 18.9 (CH_3), 24.5 (br, B–CH), 56.7 (OCH_3), 114.3 (CH), 116.1 (CH), 124.6 (CH), 130.8 (CH), 137.6 (C), 150.7 (C), 160.2 (C). $^{11}B\{^1H\}$ NMR: 34.6 (br).

Catalytic Hydroboration of 15b: (a) Synthesis of 17b. ^{1}H NMR: δ 1.55 (d, J = 8 Hz, 3 H, CH_3), 2.95 (q, J = 8 Hz, 1 H, CH), 6.97–7.05 (ov m, 4 H, cat), 7.17–7.31 (ov m, 4 H, Ph). ^{13}C NMR: 17.5 (CH_3), 25.0 (br, B–CH), 113.0 (CH), 115.8 (d, J_{CF} = 21 Hz, CH), 123.4 (CH), 130.1 (d, J_{CF} = 8 Hz, CH), 140.3 (d, J_{CF} = 3 Hz, C), 149.3 (C), 160.1 (d, J_{CF} = 243 Hz, C). $^{11}B\{^1H\}$ NMR: 34.4 (br).

Catalytic Hydroboration of 15c: Synthesis of 17c. ^{1}H NMR: δ 1.57 (d, J = 8 Hz, 3 H, CH_3), 2.95 (q, J = 8 Hz, 1 H, CH), 7.01–7.27 (ov m, 4 H, Ph), 7.42 (ov m, 4 H, cat). ^{13}C NMR: 14.5 (CH_3), 25.7 (br, B–CH), 112.8 (CH), 123.2 (CH), 129.3 (CH), 130.1 (CH), 131.5 (C), 143.4 (C), 148.7 (C). $^{11}B\{^1H\}$ NMR: 34.6 (br).

Catalytic Hydroboration of 15d: Synthesis of 17d. ^{1}H NMR: δ 1.55 (d, J = 8 Hz, 3 H, CH_3), 2.95 (q, J = 8 Hz, 1 H, CH), 6.97–7.05 (ov

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m, 4 H, cat), 7.16-7.21 (ov m, 2 H, Ph), 7.27-7.32 (ov m, 2 H, Ph). ^{13}C NMR: 17.0 (CH_3), 25.6 (br, B-CH), 113.1 (CH), 113.3 (CH), 115.5 (d, J_{CF} = 21 Hz, CH), 123.4 (CH), 124.5 (CH), 130.7 (d, J_{CF} = 8 Hz, CH), 147.3 (d, J_{CF} = 3 Hz, C), 149.2 (C), 164.0 (d, J_{CF} = 244 Hz, C). $^{11}B\{^1H\}$ NMR: 35.2 (br).

Catalytic Hydroboration of 15e: Synthesis of 17e. ^1H NMR: δ 1.70 (d, J = 8 Hz, 3 H, CH_3), 3.13 (q, J = 8 Hz, 1 H, CH), 6.96-7.02 (ov m, 2 H, cat), 7.16-7.21 (ov m, 2 H, cat), 7.34-7.40 (ov m, 2 H, Ph), 7.48-7.51 (ov m, 1 H, Ph), 7.78 (br m, 4 H, Ph). ^{13}C NMR: 17.1 (CH_3), 26.0 (br, B-CH), 113.0 (CH), 123.3 (CH), 125.8 (CH), 126.5 (CH), 126.6 (CH), 127.8 (CH), 128.2 (CH), 128.3 (CH), 128.8 (CH), 133.1 (C), 134.9 (C), 142.1 (C), 149.4 (C). $^{11}B\{^1H\}$ NMR: 35.5 (br).

Catalytic Hydroboration of 18: Synthesis of 20. ^1H NMR: δ 0.96 (t, J = 7 Hz, 3 H, CH_3), 1.92, 2.15 (m, J = 7 Hz, 1 H, CH_2), 2.74 (d d, J = 7 Hz, 1 H, CH), 6.98-7.27 (ov m, 9 H, Ph and cat). ^{13}C NMR: 14.1 (CH_3), 26.2 (CH_2), 34.8 (br, B-CH), 112.9 (CH), 123.2 (CH), 126.3 (CH), 129.1 (CH), 129.3 (CH), 142.6 (C), 149.1 (C). $^{11}B\{^1H\}$ NMR: 34.6 (br).

Catalytic Hydroboration of 21: Synthesis of 23. ^1H NMR: δ 2.39 (d d, J = 8 Hz, 2 H, CH_2), 3.02 (ov m, J = 8 Hz, 2 H, CH_2), 3.23 (dd, J = 8 Hz, 1 H, CH), 6.99-7.15 (ov m, 4 H, cat), 7.18-7.21 (ov m, 3 H, Ph), 7.39-7.42 (m, 1 H, Ph). ^{13}C NMR: 28.9 (CH_2), 30.8 (br, B-CH), 33.8 (CH_2), 113.0 (CH), 123.3 (CH), 125.0 (CH), 125.3 (CH), 128.7 (CH), 128.9 (CH), 144.4 (C), 144.6 (C), 149.3 (C). $^{11}B\{^1H\}$ NMR: 34.8 (br).

Catalytic Hydroboration of 24: (a) Synthesis of 25. ^1H NMR: δ 1.22 (d, J = 8 Hz, 3 H, CH_3), 1.65 (ov m, J = 8 Hz, 2 H), 3.26 (sext, J = 8 Hz, 1 H), 6.97-7.30 (ov m, 9 H). ^{13}C NMR: 21.7 (br, B-CH_2), 25.3 (CH_3), 36.6 (CH), 113.0 (CH), 123.4 (CH), 126.8 (CH), 127.3 (CH), 129.3 (CH), 149.4 (C), 149.7 (C). $^{11}B\{^1H\}$ NMR: 35.0 (br).

(b) Synthesis of 26. ^1H NMR: δ 1.58 (s, 6 H, CH_3), 6.98-7.44 (ov m, 9 H, Ph and cat). ^{13}C NMR: 22 (br, B-C), 26.2 (CH_3), 113.1 (CH), 123.4 (CH), 126.3 (CH), 127.2 (CH), 129.1 (CH), 148.0 (C), 149.3 (C). $^{11}B\{^1H\}$ NMR: 35.4 (br).

Catalytic Hydroboration of 27: Synthesis of 28. ^1H NMR: δ 1.26, 2.69 (t, J = 8 Hz, 2 H, CH_2), 1.94 (m, J = 8 Hz, 2 H, CH_2), 6.95-7.28 (ov m, 9 H, Ph and cat). ^{13}C NMR: 10 (br, B-CH_2), 25.6 (CH_2), 38.0 (CH_2), 112.0 (CH), 122.2 (CH), 125.5 (CH), 128.2 (CH), 128.4 (CH), 142.0 (C), 148.4 (C). $^{11}B\{^1H\}$ NMR: 34.4 (br).

Catalytic Hydroboration of 29a: Synthesis of 30a. ^1H NMR: δ 0.91 (m, 3 H, CH_3), 1.37 (ov m, 12 H, CH_2), 1.69 (m, 2 H, CH_2), 7.02 (m, 2 H, cat), 7.21 (m, 2 H, cat). ^{13}C NMR: 11.4 (br, B-CH_2), 14.5 (CH_3), 23.6 (CH_2), 24.7 (CH_2), 30.2 (CH_2), 30.4 (CH_2), 32.9 (CH_2), 33.2 (CH_2), 112.8 (CH), 123.1 (CH), 149.5 (C). $^{11}B\{^1H\}$ NMR: 35.1 (br).

Catalytic Hydroboration of 29b: Synthesis of 30b. ^1H NMR: δ 0.81 (s, 9 H, CH_3), 1.20 (m, J = 8 Hz, 2 H, CH_2), 1.54 (m, J = 8 Hz, 2 H, CH_2), 6.87 (m, 2 H, cat), 7.01 (m, 2 H, cat). ^{13}C NMR: 5.2 (br, B-CH_2), 29.4 (CH_3), 31.2 (C), 38.3 (CH_2), 112.8 (CH), 123.3 (CH), 149.1 (C). $^{11}B\{^1H\}$ NMR: 35.5 (br).

Catalytic Hydroboration of 29c: Synthesis of 30c. ^1H NMR: δ 0.03 (s, 9 H, CH_3), 0.81 (m, J = 8 Hz, 2 H, CH_2), 1.23 (m, J = 8 Hz, 2 H, CH_2), 6.88 (m, 2 H, cat), 7.04 (m, 2 H, cat). ^{13}C NMR: -1.9 (CH_3), 4.1 (br, B-CH_2), 9.9 (CH_2), 112.9 (CH), 122.8 (CH), 149.4 (C). $^{11}B\{^1H\}$ NMR: 35.5 (br).

Catalytic Hydroboration of 31: Synthesis of 32. ^1H NMR: δ 0.92 (d, J = 7 Hz, 6 H, CH_3), 1.12 (s, 6 H, CH_3), 1.77 (m, J = 7 Hz, 1 H, CH), 7.02 (m, 2 H, cat), 7.19 (m, 2 H, cat). ^{13}C NMR: 28 (v br, B-C), 19.1 (CH_3), 22.5 (CH_3), 36.4 (CH), 112.3 (CH), 122.9 (CH), 149.3 (C). $^{11}B\{^1H\}$ NMR: 35.5 (br).

Acknowledgment. We thank Nancy J. Herling, John E. Feaster, Elwood A. Conaway, Yi Meng, Fred Davidson, John Nguyen, and Keith D. Raffell for expert technical assistance and Dr. Mark J. Burk (DuPont) for many valuable discussions. We also thank the referees for several helpful comments. T.B.M. acknowledges support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Natural Sciences and Engineering Research Council of Canada.

Supplementary Material Available: ^1H NMR, ^{11}B NMR, and ^{13}C NMR spectra at 25 °C in THF-d_8 of **17a** using **1**, **20** using **9**, and **32** using **12** (t = 40 h) (13 pages). Ordering information is given on any current masthead page.

Asymmetric [2 + 2] Cycloaddition Reaction Catalyzed by a Chiral Titanium Reagent

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Abstract: In the presence of certain Lewis acids, alkenes containing an alkylthio group (for example, ketene dithioacetals, alkenyl sulfides, alkynyl sulfides, and allenyl sulfides) react with electron deficient olefins to give the corresponding cyclobutane, cyclobutene, or methylene cyclobutane derivatives. By employing a chiral titanium catalyst generated in situ from dichlorodiisopropoxytitanium and a tartrate-derived chiral diol, the [2 + 2] cycloaddition reaction proceeds with high enantioselectivity.

The development of asymmetric reactions has been one of the main themes of modern synthetic organic chemistry, and currently much effort is being directed toward the development of catalytic asymmetric reactions.[1] Cyclopropane and cyclohexane frameworks have been constructed enantioselectively by the catalytic asymmetric cyclopropanation[2] and Diels-Alder reactions,[3] respectively. On the other hand, there exists no practical catalytic method for the synthesis of optically active cyclobutanes,[4] which hitherto have been prepared conventionally by diastereoselective reactions using chiral starting materials[5] or by optical resolution.[5a,6]

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