Reactions of Catecholborane with Wilkinson's Catalyst: Implications for Transition Metal-Catalyzed Hydroborations of Alkenes

Kevin Burgess,*,† Wilfred A. van der Donk,† Stephen A. Westcott,‡ Todd B. Marder,*,‡ R. Thomas Baker,*,§ and Joseph C. Calabrese§

Contribution from the Department of Chemistry, Texas A & M University, College Station, Texas 77843, Department of Chemistry, University of Waterloo. Waterloo. Ontario. Canada N2L 3G1. and Central Research and Development. Science and Engineering Laboratories,⊥ E. I. du Pont de Nemours and Co., Experimental Station, Wilmington, Delaware 19880-0328. *Received March 17, 1992*

Abstract: Reactions of catecholborane ($HBO_2C_6H_4$) with $RhCl(PPh_3)_3$ (**1**) yield a variety of products depending on the B/Rh ratio, solvent, and temperature. Of particular relevance to catalyzed alkene hydroboration is degradation of $HBO_2C_6H_4$ to $B_2(O_2C_6H_4)_3$/'BH_3' and the dihydride $RhH_2Cl(PPh_3)_3$ (**3**). The molecular structure of **3**, determined by X-ray diffraction, has meridional phosphine ligands and cis hydrides. Catalyst systems formed from in situ addition of PPh_3 to $[Rh(\mu\text{-}Cl)(COD)]_2$ (COD = 1,5-cyclooctadiene) are fundamentally different from Wilkinson's catalyst; $RhCl(COD)(PPh_3)$ forms initially, but the reaction of this with PPh_3 is slow. Monitoring catalyzed hydroborations using Wilkinson's catalyst and catecholborane by multinuclear NMR spectroscopy, prior to oxidative workup, showed that *alkylboranes* were formed with some sterically hindered alkenes. With 2-methylbut-2-ene (**24**), for example, we observed significant quantities of disiamylborane, $(CHMeCHMe_2)_2$, formed via addition of 'BH_3' to **24**. When excess PPh_3 was added to the catalyst system, however, the desired alkylboronate ester was formed in high yield. Partial oxidation of $RhCl(PPh_3)_3$ had a significant effect on product (and D-label) distributions. Detailed investigations of catalyzed additions of $DBO_2C_6H_4$ to allylic silyl ethers $CH_2{=}C(Me)CRR'(OSi^tBuMe_2)$ (R, R' = H, Me) demonstrated that deuterium incorporation at the carbon bonded to boron in the primary alcohol product occurs only with freshly prepared Wilkinson's catalyst or when excess PPh_3 is added to the oxidized catalyst. With freshly prepared Wilkinson's catalyst, addition of H_2 (or D_2) to these substrates is a significant competing reaction and appreciable *catalytic formation of vinylboronate esters* is also observed. The latter presumably arise via insertion of alkene into a Rh-B bond, followed by β-hydride elimination. Subsequent in situ addition of H_2 (DH or D_2) to these vinylboronate esters provides an alternative explanation to α-deuterium incorporation into the resulting primary alcohols.

Introduction

Rhodium-catalyzed addition of catecholborane[1] ($HBO_2C_6H_4$) to alkenes often proceeds with chemo-,[2,3] regio-,[2-20] and stereoselectivities[3,6-20] complementary to those of the uncatalyzed reaction employing conventional hydroborating agents such as 9-BBN.[21] A mechanism proposed for the reaction using Wilkinson's catalyst,[2,22] $RhCl(PPh_3)_3$ (**1**), involves oxidative addition of the B-H bond to Rh(I), followed by alkene insertion into the Rh-H bond and subsequent reductive elimination of the B-C bond (Scheme I).

To date, little evidence has been published to confirm or refute the mechanism outlined in Scheme I. Several stoichiometric reactions of boron hydrides with organometallic complexes have been described and may be analogous to some of the steps involved in the Wilkinson's catalyst/catecholborane system.[23-26] Evans and Fu performed a series of deuterium labeling experiments in which four substrates were each treated with 0.1 equiv of catecholborane-*d*.[4] The presence of label in the recovered starting material was taken as evidence for reversibility of migratory insertion of alkenes into Rh-H(D) bonds. Other conclusions regarding the mechanism were made on the basis of label distribution in the product. More recently, two of us[27] questioned these conclusions on the grounds that competing processes could influence the deuterium label distributions. Furthermore, different label distributions were observed when these reactions were repeated by Burgess and van der Donk.[27] However, the product and label distributions reported in this study were obtained using commercial, partially oxidized catalyst.[37]

The work presented here describes the use of multinuclear NMR spectroscopy to investigate reactions of catecholborane with $RhCl(PPh_3)_3$. Detailed examination of product and label distributions provides additional mechanistic insight into catalyzed alkene hydroborations. Evidence will be presented that indicates

† Texas A & M University.
‡ University of Waterloo.
§ E.I. du Pont de Nemours and Co.
⊥ Contribution No. 6140 from du Pont.

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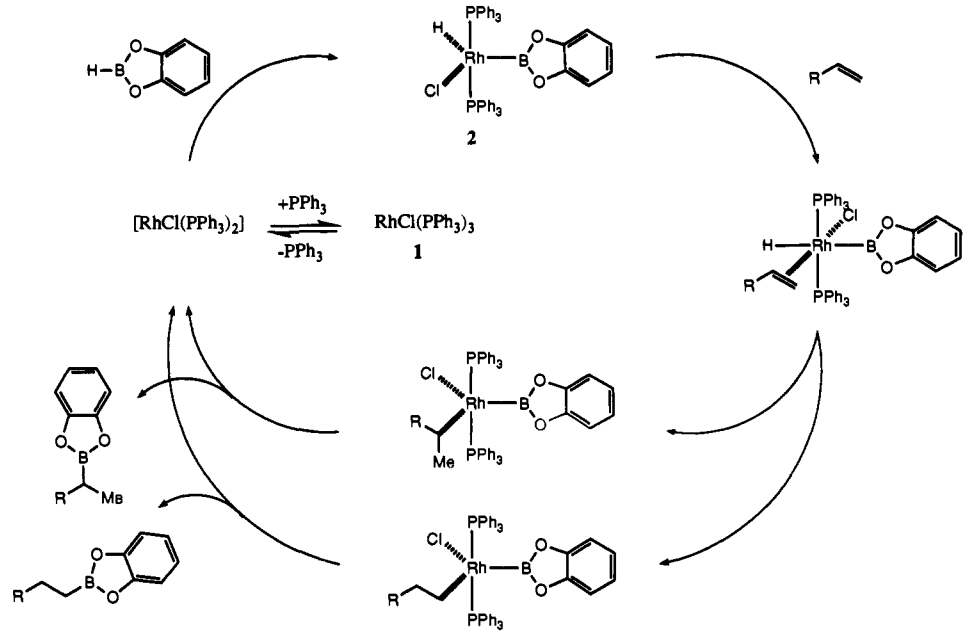
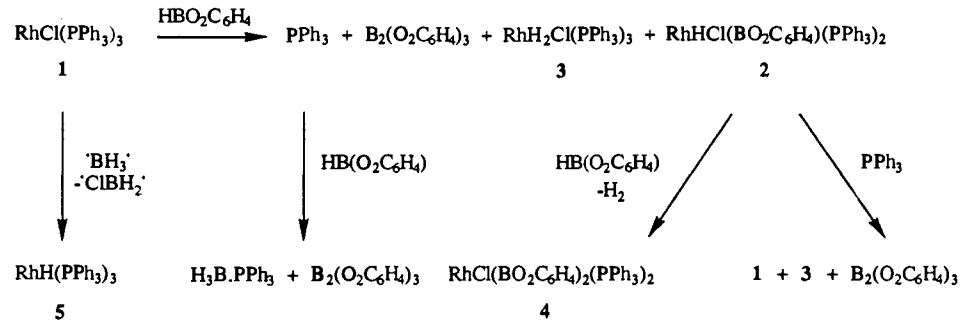
Scheme I. A Possible Mechanism for Alkene Hydroborations Mediated by $RhCl(PPh_3)_3$



Scheme II. Reaction of $RhCl(PPh_3)_3$ with Catecholborane



that (i) the catecholborane/$RhCl(PPh_3)_3$ hydroborating system is complex, affording several phosphinorhodium and boron-containing products arising from rhodium-mediated degradation of catecholborane; (ii) hydroborations of sterically demanding (slow reacting) alkenes give appreciable amounts of hydrogenation and/or BH_3-derived products from degradation of catecholborane; (iii) the label distributions reported by Evans and Fu[4] are reproducible when the catalyst system is prepared and manipulated under anaerobic conditions, and the deuterium label distributions first reported by Burgess and van der Donk[27] are attributed to partial oxidation of the catalyst; (iv) α-deuteration in the hydroboration of 2-methyl-3-((*tert*-butyldimethylsilyl)oxy)but-1-ene (**30**) is accompanied by significant amounts of aldehyde formed via oxidation of vinylboronate esters, whereas only alcohol product (and no α-deuteration) is obtained if oxidized Wilkinson's catalyst is used; and (v) in situ addition of D_2 (from $DBO_2C_6H_4$) to vinylboronate esters would account for α-deuterium incorporation in the product alcohol.

Results and Discussion

Reactions of Catecholborane with $RhCl(PPh_3)_3$ (1). Two groups have reported that catecholborane reacts with **1** to give $RhHCl(BO_2C_6H_4)(PPh_3)_2$ (**2**).[2,28] We reinvestigated this reaction using multinuclear NMR spectroscopy for a variety of solvents and catecholborane/Wilkinson's catalyst ratios and found that the system is more complicated than was implied previously. Moderate yields of the oxidative addition product $RhHCl(BO_2C_6H_4)(PPh_3)_2$ (**2**) were obtained via slow addition of catecholborane (5 equiv) to solutions of Wilkinson's catalyst in either THF or CH_2Cl_2, but several other compounds were also formed (Scheme II). The major phosphinorhodium complexes present were **2**, $RhH_2Cl(PPh_3)_3$ (**3**),[29] and a new compound containing two Rh–BR_2 moieties, $RhCl(BO_2C_6H_4)_2(PPh_3)_2$ (**4**). Substantial quantities of $H_3B{\cdot}PPh_3$, $B_2(O_2C_6H_4)_3$, and free PPh_3 were also observed. Reactions of **1** and catecholborane in toluene were even more complicated and gave trace amounts of $RhH(PPh_3)_3$ (**5**), presumably via chloride abstraction by BH_3. The molecular structure of hydride **5**, determined by X-ray diffraction, was similar to that reported previously for the dimethylamine solvate (see supplementary material).[30] We were unable to obtain single crystals of **2** suitable for X-ray analysis, but the analogous complex $RhHCl(BO_2C_6H_4)(P^iPr_3)_2$ has been characterized structurally in other work.[26] The molecular structure of $RhH_2Cl(PPh_3)_3$ (**3**) was also determined by X-ray diffraction (Figure 1, Table I); it has meridional PPh_3 ligands and cis hydrides, as proposed previously on the basis of solution NMR studies.[29]

Monitoring reaction of **1** with 3 equiv of catecholborane in THF by multinuclear NMR spectroscopy provided additional details

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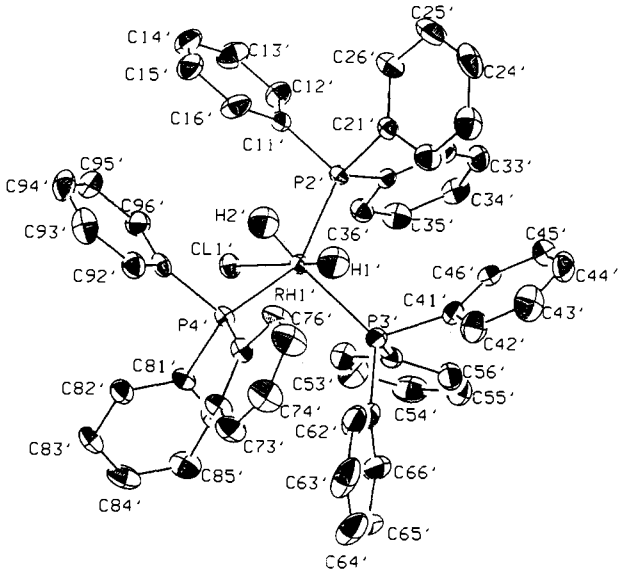


Figure 1. ORTEP plot (50% probability ellipsoids) of $RhH_2Cl(PPh_3)_3$ (**3**). Selected bond distances and angles: Rh–Cl(1) = 2.501 (1) Å, Rh–P(2) = 2.302 (1) Å, Rh–P(3) = 2.458 (1) Å, Rh–P(4) = 2.331 (1) Å, Cl(1)–Rh–P(2) = 87.52 (5)°, Cl(1)–Rh–P(3) = 100.81 (5) Å, Cl(1)–Rh–P(4) = 87.08 (5)°, P(2)–Rh–P(3) = 100.87 (5)°, P(2)–Rh–P(4) = 150.90 (5)°, P(3)–Rh–P(4) = 108.23 (5)°.

of product formation. Initially, the only new phosphinorhodium complex detected in solution was oxidative addition product **2**. Within minutes, however, dihydride **3** and bis(boryl) complex **4** were observed. This implies that excess catecholborane reacts with **2** to give $RhCl(BO_2C_6H_4)(PPh_3)_2$ (**4**) and dihydrogen, which is then trapped by **1** to afford dihydride **3** (eqs 1, 2). Indeed, addition of catecholborane to isolated **2** gave **4** in high yield.

$$\underset{\mathbf{2}}{RhHCl(BO_2C_6H_4)(PPh_3)_2} + HBO_2C_6H_4 \rightarrow \underset{\mathbf{4}}{RhCl(BO_2C_6H_4)(PPh_3)_2} + H_2 \quad (1)$$

$$\underset{\mathbf{1}}{RhCl(PPh_3)_3} + H_2 \rightleftarrows \underset{\mathbf{3}}{RhH_2Cl(PPh_3)_3} \quad (2)$$

Finally, after several days we observed partial regeneration of starting complex **1** and increasing amounts of dihydride **3** and $B_2(O_2C_6H_4)_3$. The reappearance of $RhCl(PPh_3)_3$ suggests that addition of $HBO_2C_6H_4$ to **1** may be *reversible* under some conditions (eq 3). This was confirmed by reaction of isolated **2** with

$$\underset{\mathbf{1}}{RhCl(PPh_3)_3} + HBO_2C_6H_4 \rightleftarrows \underset{\mathbf{2}}{RhHCl(BO_2C_6H_4)(PPh_3)_2} + PPh_3 \quad (3)$$

1 equiv of PPh_3, which gave **1**, **3**, $B_2(O_2C_6H_4)_3$, and a small amount of bis(boryl) complex **4** (from reaction of liberated $HBO_2C_6H_4$ with **2**). The eventual formation of greater amounts of dihydride **3** (relative to **4**) and $B_2(O_2C_6H_4)_3$ in these reactions reveals an additional pathway involving *irreversible Rh-mediated degradation of catecholborane* (eq 4). While we do not know

$$\underset{\mathbf{1}}{RhCl(PPh_3)_3} + nHBO_2C_6H_4 \rightarrow \underset{\mathbf{3}}{RhH_2Cl(PPh_3)_3} + B_2(O_2C_6H_4)_3 \quad (4)$$

the detailed stoichiometry of eq 4, similar nucleophile-promoted $HBO_2C_6H_4$ degradation reactions have been reported,[31,32] and we have found[33] that PPh_3 and $HBO_2C_6H_4$ slowly give $B_2(O_2C_6H_4)_3$ and $H_3B{\cdot}PPh_3$ (eq 5).

$$PPh_3 + 3HBO_2C_6H_4 \rightarrow H_3B{\cdot}PPh_3 + B_2(O_2C_6H_4)_3 \quad (5)$$

In summary, reactions of catecholborane with Wilkinson's catalyst involve a complex series of equilibria which lead eventually to irreversible formation of $B_2(O_2C_6H_4)_3$, 'BH_3', and H_2 (Scheme II). We will see later the implications of this chemistry for catalyzed hydroborations using **1**.

Table I

	3·THF	5·2THF
formula	$C_{58}H_{55}ClOP_3Rh$	$C_{62}H_{62}O_2P_3Rh$
fw	927.25	1035.01
cryst syst	triclinic	orthorhombic
a, Å	12.426 (1)	9.637 (2)
b, Å	12.432 (1)	21.110 (4)
c, Å	34.511 (8)	25.194 (4)
β, deg	96.14 (1)	
γ, deg	119.60 (1)	
V, Å^3	4558.1	5125.4
Z	4	4
ρ_{calcd}, g cm^{-3}	1.415	1.340
space group	$P\bar{1}$ (No. 2)	$P2_12_12_1$ (No. 19)
cryst dimens, mm	0.32 × 0.15 × 0.45	0.23 × 0.22 × 0.50
temp, °C	−70	−70
radiation	Mo Kα	Mo Kα
μ, cm^{-1}	5.69	4.61
data coll method	ω	ω
max 2θ, deg	48.0	52.0
scan speed, (deg/min)	1.50–5.00	1.70–4.00
scan width (deg)	1.20–1.80ω	1.20–1.50ω
total no. of obsvns	15690	5611
no. of unique data ($I > 3\sigma(I)$)	9022	3137
final no. of variables	1113	591
final Δ/ρ	0.01	0.06
max residual density, e/Å^3	0.46	0.50
R^a	0.037	0.064
$R_w{}^b$	0.038	0.058
GOF^c	1.38	1.37

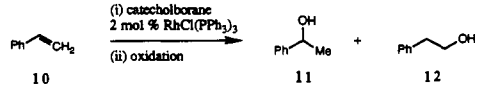
$^a \sum||F_o| - |F_c||/\sum|F_o|$. $^b [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. $^c [\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$.

Parenthetically, we note that frequently used hydroboration catalyst mixtures formed from in situ addition of PPh_3 to $[Rh(\mu\text{-}Cl)(COD)]_2$ (**6**) are also complex. As observed by ^{31}P NMR, $RhCl(COD)(PPh_3)$ (**7**) formed rapidly upon addition of 1 equiv of PPh_3 to **6**. However, conversion of COD complex **7** into Wilkinson's catalyst was incomplete after 24 h at 25 °C, even with 8 equiv of PPh_3.[34] When catecholborane was added to the system, a very complex mixture resulted. For instance, addition of 8 equiv of triphenylphosphine to $[Rh(\mu\text{-}Cl)(COD)]_2$ followed immediately by 60 equiv of catecholborane gave a gross mixture of products. Minor amounts of oxidative addition product **2** and dihydride **3** were detected, and most of the added PPh_3 was converted to $H_3B{\cdot}PPh_3$. This reaction mixture also contained several PPh_2-bridged complexes (presumably due to rhodium-mediated P–C bond cleavage)[35] which were characterized by triplet of multiplet ^{31}P resonances at ca. 84 ppm (J_{RhP} = 85 Hz). Many phosphinorhodium species were present, and $H_3B{\cdot}PPh_3$ remained by far the predominant product when a solution of **6** and PPh_3 (8 equiv) was allowed to stir for 40 min prior to addition of excess catecholborane. Formation of PPh_2-bridged complexes in this reaction was minimal. In situ addition of PPh_3 to $[Rh(\mu\text{-}Cl)(COD)]_2$ (**6**) does *not* give Wilkinson's catalyst exclusively, and it may therefore behave differently in catalysis.

Reactions of Catecholborane with $RhCl(PPh_3)_3$ (1) and Alkenes. The transformations described above relate to the catalyzed hydroboration system without substrate. What is the influence of alkenes on these interdependent processes? NMR studies of 1-octene, catecholborane, and $RhCl(PPh_3)_3$ (1:1:0.02 ratio) in THF-d_8 at −40 °C indicated that comparable amounts of oxidative addition product **2** and dihydride **3** were formed with concomitant formation of $B_2(O_2C_6H_4)_3$. Complex **3** is a catalyst precursor for *hydrogenation* reactions, thus accounting for competing alkene reduction in catalyzed hydroborations.

Early work by Männig and Nöth indicated that $RhHCl(BO_2C_6H_4)(PPh_3)_2$ (**2**) reacts with alkenes to give alkylboronate esters and $[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$ (**8**).[2] We confirmed this observation and found that **8** and catecholborane regenerated oxidative addition product **2** in high yield. Further addition of excess cate-

Table II. Catalyzed Hydroborations of Phenylethene



entry	catalyst[a]	additions	11:12
1	$RhCl(PPh_3)_3$[16]		10:90
2	$RhCl(PPh_3)_3$[4]		100:0
3	$RhCl(PPh_3)_3$[27]		20:80
4	$RhCl(PPh_3)_3$ (A)		>99:<1
5	$RhCl(PPh_3)_3$ (B)		24:76
6	$RhCl(PPh_3)_3$ (A)	O_2	60:40
7	$RhCl(PPh_3)_3$ (B)	PPh_3	>99:<1
8	$RhCl(O_2)(PPh_3)_3$		>99:<1
9	$RhCl(O_2)(PPh_3)_3$	O_2	14:86
10	$[Rh(COD)Cl]_2$[20]	2 PPh_3	41:59
11	$[Rh(COD)Cl]_2$[20]	4 PPh_3	98:2

[a] Preparation A via the *Inorganic Syntheses* procedure, handled and manipulated under anaerobic conditions; preparation B is catalyst stored and manipulated in the air.

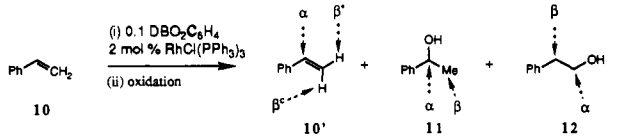
cholborane slowly gave bis(boryl) complex **4**. As alkenes react faster with **2** than does catecholborane, bis(boryl) complex **4** was not detected under catalytic conditions. Complexes **2** and **4** were shown also to be catalyst precursors for the hydroboration reaction. For bis(boryl) complex **4**, this suggests that boryl transfer to alkene may occur via insertion of alkene into the Rh–B bond. In fact, complex **4** reacts stoichiometrically with some unsaturated substrates, transferring both boryl groups and regenerating $[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$ (**8**).[36a]

Catalyzed Hydroborations of Phenylethene. Catalyzed hydroborations of phenylethene give predominantly 1-phenylethanol (after oxidative workup) if the catalyst is handled and manipulated under anaerobic conditions.[4,20,32,37] Formation of primary alcohol[15,27] has been attributed to partial oxidation of the catalyst.[37] Conflicting results reported for the regioselectivity (see Table II, entries 1–3) and distribution of deuterium in labeling studies using catecholborane-*d* ($DBO_2C_6H_4$)[4,27] are due to varying degrees of catalyst oxidation.[37]

While the chemistry associated with oxidation of $RhCl(PPh_3)_3$ in the solid state is unclear, in solution it is known to give $RhCl(O_2)(PPh_3)_3$ (**9**), which decomposes to $[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$ (**8**), $[RhCl(O_2)(PPh_3)_2]_2$, and triphenylphosphine oxide.[38,39] Further oxidation presumably follows the same trend, lowering the phosphine to rhodium ratio by converting more triphenylphosphine to its oxide. Oxidized $RhCl(PPh_3)_3$ is known to have different properties from the parent material;[40–42] significantly, it is a more active catalyst for alkene hydrogenations.[43] Partial oxidation of $RhCl(PPh_3)_3$ was also the cause of disparate results in deuterium labeling studies of alkene hydrogenation reactions reported over two decades ago.[44,45]

Formation of **9** alone does not account for the change in regioselectivity as hydroboration of phenylethene catalyzed by pure, isolated **9** gave, after oxidation, almost exclusively 1-phenylethanol (**11**) (Table II, entry 8). Primary alcohol **12** was the major product, however, when catalyst **9** was stirred for 1 h at 25 °C in THF under argon before phenylethene and catecholborane were added. Increasing amounts of 2-phenylethanol (**12**) were produced when a small amount of oxygen was introduced into the atmosphere above the hydroboration mixture (using either **1** or its dioxygen derivative **9** as catalyst, entries 6 and 9). Consequently, formation of the primary alcohol **12** appears to be due to complexes other than $RhCl(PPh_3)_3$ and $RhCl(O_2)(PPh_3)_3$. Higher selectivity for the secondary alcohol was observed when triphenylphosphine was added to oxidized catalyst (entry 7); Dai and co-workers have reported increased selectivity as more phosphine was added to $[Rh(\mu\text{-}Cl)(COD)]_2$ catalyst for the same reaction (entries 10 and 11).[20] All these observations are consistent with oxidative removal of triphenylphosphine in solution causing increased selectivity for the primary alcohol **12**.[46]

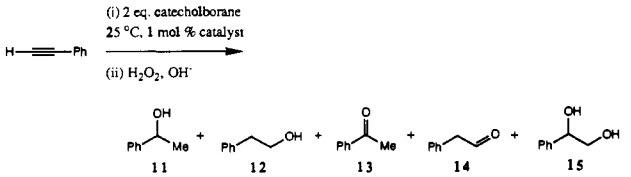
Table III. Labeling Experiments in Catalyzed Hydroborations of Phenylethene



product/label distribution	catalyst system[a] $RhCl(PPh_3)_3$ (A)	$RhCl(PPh_3)_3$ (B)	$RhCl(PPh_3)_3$ (B) + 3 PPh_3
10′:11:12	trace: >98:<2	40:14:46	trace: ~96:~4
10′; α:β^c:β^t	2:49:49	10:45:45	4:48:48
11; α:β	0:100	0:100	0:100
12: α:β	0:100	40:60	0:100

[a] Preparation A via the *Inorganic Syntheses* procedure, handled and manipulated under anaerobic conditions; preparation B is catalyst stored and manipulated in the air.

Table IV. Effect of Catalyst in Rhodium-Mediated Hydroborations of Phenylethyne



entry	catalyst[a]	reaction time (h)	product distribution (%)[b] 11	12	13	14	15
1	$RhCl(PPh_3)_3$	1.0	9	12	32	47	trace
2	$RhCl(PPh_3)_3$ + PPh_3	1.5	2	3	35	60	trace
3	$RhCl(PPh_3)_3$	12	20	9	10	3	58
4	$RhCl(PPh_3)_3$ + PPh_3	15	29	9	16	17	29
5	$[Rh(COD)Cl]_2$ + 8PPh_3	12	54	19	trace	trace	27

[a] Prepared and handled under anaerobic conditions. [b] Determined via ^1H NMR, ratios vary with reaction conditions.

Table III shows results obtained for catalyzed hydroborations of phenylethene with 0.1 equiv of $DBO_2C_6H_4$ in the presence of Wilkinson's catalyst (**1**) that was (i) freshly prepared, (ii) exposed to air in the solid state, and (iii) oxidized and then added to 3 equiv of PPh_3. Reactions mediated by oxidized catalyst in the absence of added PPh_3 gave more primary alcohol **12** and more deuterium incorporation in the recovered starting material (**10′**) relative to analogous reactions using freshly prepared catalyst.

Relatively large amounts of hydrogenation product have been isolated in catalyzed "hydroborations" of some other substrates, but reactions of phenylethene mediated by pure $RhCl(PPh_3)_3$ gave only approximately 5% phenylethane.

Hydroboration of Phenylethyne. Catalyzed hydroborations of phenylethyne with 2 equiv of catecholborane gave, after oxidation, carbonyl compounds, alcohols, and/or diols, depending on reaction conditions (Table IV). At short reaction times isomeric carbonyl compounds predominated (entries 1 and 2), whereas extended periods favored formation of alcohols (entries 3–5). Formation

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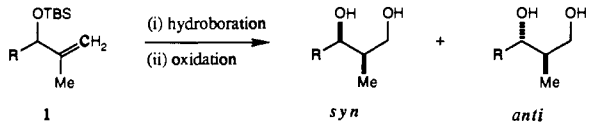
(40) Augustine, R. L.; Peppen, J. F. V. *J. Chem. Soc., Chem. Commun.* **1970**, 497.
(41) Augustine, R. L.; Peppen, J. V. *J. Chem. Soc., Chem. Commun.* **1970**, 497.
(42) Augustine, R. L.; Peppen, J. F. V. *J. Chem. Soc., Chem. Commun.* **1970**, 495.
(43) Bekkum, H. van; Rantwijk, F. van; Putte, T. van der *Tetrahedron Lett.* **1969**, 1.
(44) Morandi, J. R.; Jensen, H. B. *J. Org. Chem.* **1969**, *34*, 1889.
(45) Hussey, A. S.; Takeuchi, Y. *J. Am. Chem. Soc.* **1969**, *91*, 672.
(46) We cannot rule out involvement of heterogeneous catalysis in some of the reactions where oxidized **1** is involved.
(47) Osborn, J. A.; Wilkinson, G.; Mrowca, J. J. *Inorg. Synth.* **1972**, *10*, 67.
(48) Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1990**, *28*, 77.

of primary alcohol **12** originates presumably from hydrogenation of intermediate vinylboronate esters, as the alternative, hydroboration of phenylethene, would give secondary alcohol **11** exclusively (vide supra).

To test for *hydrogenation* of vinylboronate esters under catalyzed hydroboration conditions, a vinylboronate ester was prepared and isolated from the uncatalyzed reaction of 1-hexyne with catecholborane. When this vinylboronate ester was subjected to catalytic hydroboration, the resulting mixture indeed contained significant amounts of 1-hexanol (after oxidation).

Formation of diol **15** in the catalyzed hydroboration of phenylethyne (Table IV) is interesting because it suggests that vinylboronate ester intermediates can be hydroborated catalytically. Direct evidence for this type of transformation has been obtained in experiments with an allylsilyl ether substrate (vide infra).

Hydroborations of Unsaturated Silyl Ethers I. Catalyzed hydroborations of substrate type **I** and related compounds are stereocomplementary to the uncatalyzed hydroborations. Consequently, this is probably the most important reaction category to emerge from this area so far. Burgess and Ohlmeyer suggested



catalyzed hydroborations favor the syn product
uncatalyzed hydroborations favor the anti product

that the origin of this difference between catalyzed and uncatalyzed hydroborations might be due to stereoelectronic effects in the formation of diastereomeric alkene–rhodium π-complexes.[1] This hypothesis is based upon assumptions concerning the relative rates of various steps in the presumed mechanism for catalyzed hydroboration (Scheme I), and any mechanistic insight into this particular reaction would be extremely valuable.

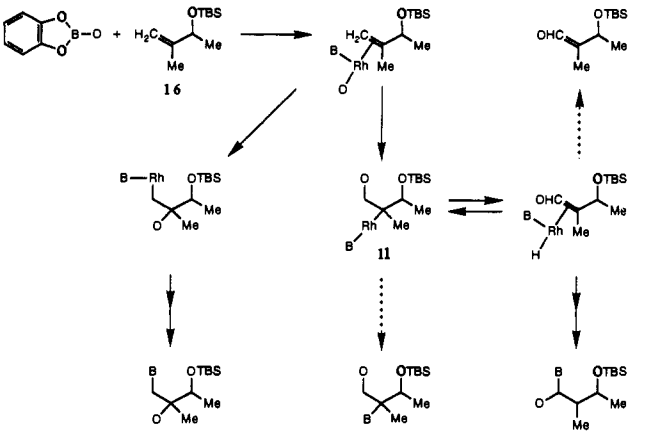
Evans and Fu found that hydroborations of 2-methyl-3-((*tert*-butyldimethylsilyl)oxy)but-1-ene (**16**, i.e., I with R = Me) using Wilkinson's catalyst and 0.1 equiv of $DBO_2C_6H_4$ gave no deuterium in the recovered alkene and ca. 17% α-deuterium incorporation in the resulting primary alcohol.[4] Conversely, Burgess et al. reported ca. 1% of the deuterium in the recovered alkene, <1% α-deuteration, and >99% β-deuteration,[27] but the catalyst used was later found to be partially oxidized.

In the present work, reinvestigation of these studies revealed that freshly prepared $RhCl(PPh_3)_3$ manipulated in an inert atmosphere indeed gave significant α-deuteration. However, in experiments using 0.1 equiv of catecholborane-*d* most of the label was found in compound **19** (Table V, entry 1), presumably derived via addition of D_2 to the alkene; *the hydroboration product was not the major product*. The reaction with 2.0 equiv of catecholborane-*d* gave a 50% yield of hydroboration product **17** in the crude reaction mixture. Significant amounts of unlabeled *aldehyde* **18** were formed whenever α-deuterium was observed in alcohol **17**. Aldehyde **18** was not present in the reaction mixture before oxidation with alkaline hydrogen peroxide (by GC analysis).

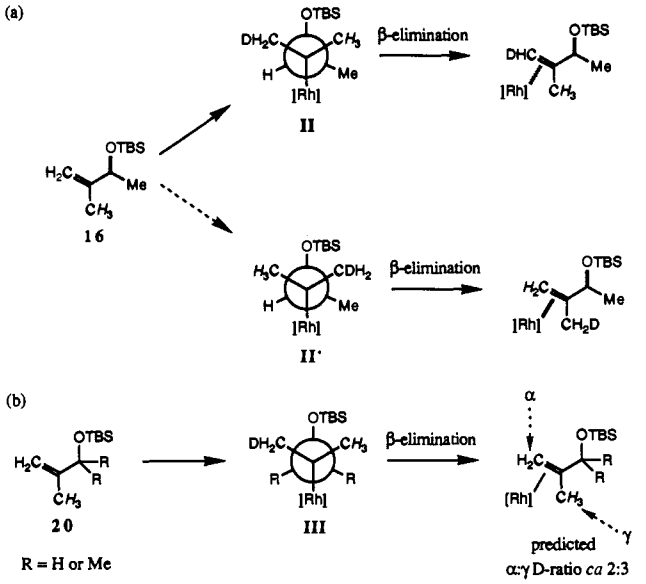
Product and label distributions changed dramatically when $RhCl(PPh_3)_3$ was allowed to react with trace amounts of oxygen (Table V, entry 2), even though the amount of oxygen added was so small that the ^{31}P NMR spectrum of this solution did not reveal any new features.[49] Neither aldehyde formation nor α-deuteration was observed to any extent in reactions using this catalyst, and the hydroboration product **17** was formed in high yield. Addition of 1 equiv of PPh_3 to the oxidized catalyst system (entry 6) restored

(49) Wilkinson's catalyst handled and prepared under rigorous conditions can contain both rhodium(II)[82] and rhodium(III)[83] contaminants. In some of the processes studied here it is conceivable that some impurity promotes side reactions, and exposure of the catalyst to air oxidizes this impurity leaving the relatively robust $RhCl(PPh_3)_3$ intact. Trace impurities (rhodium-containing or just excess phosphine) in "clean" Wilkinson's catalyst therefore could have a bearing on some of the results observed (e.g., in D-labeling studies). We briefly investigated $RhCl(PPh_3)_3$ prepared from $RhCl(PPh_3)_2(n\text{-}C_2H_4)$, and from $[Rh(n\text{-}C_2H_4)Cl]_2$[83] in the hydroboration of substrate **16**. Wilkinson's catalyst from these starting materials gives essentially the same results as that prepared from $RhCl_3$.

Scheme III. Evans/Fu Rationale for α-Deuterium Incorporation in the Hydroboration of Substrate **16**

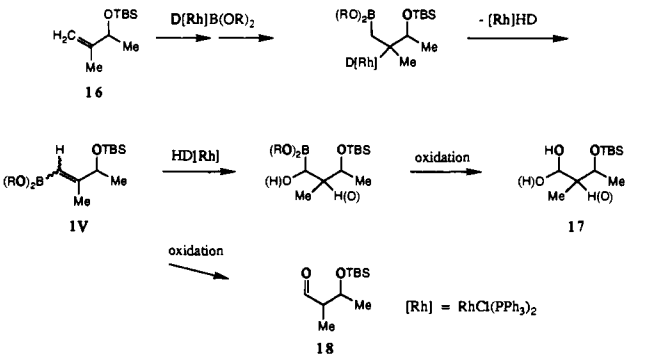


Scheme IV[a]



[a] (a) Label distributions in the catalyzed hydroboration of substrate **16** indicate that intermediate II′ cannot be present if β-elimination from II is 100% stereoselective. (b) The consequence of intermediate III in hydroboration of **20** would be a ca. 2:3 α:γ ratio of deuterium distribution.

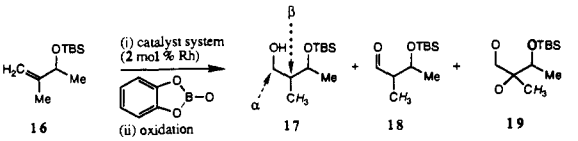
Scheme V. Possible Role of Dehydrogenative Borylation in the Catalyzed Hydroboration of Substrate **16**



the selectivity characteristic of freshly prepared **1**, i.e., α-deuterium and aldehyde formation were observed. Increased aldehyde formation and α-deuterium incorporation into product **17** were observed when 1 equiv of PPh_3 was added to freshly prepared $RhCl(PPh_3)_3$ (compare entries 3 and 5).

The data presented in Table V also show that syn:anti diastereoselectivities decrease as the proportion of α-deuterium label

Table V. Catalyzed Hydroboration of Silyl Ether **16** with Catecholborane-*d*



entry	catalyst system (method)[a]	equiv $C_6H_4O_2BD$	17:18:19[b]	D-label[c] 17; α:β	17[b] syn:anti
1	$RhCl(PPh_3)_3$ (A)	0.1	35:5:60	16:84	85:15
2	$RhCl(PPh_3)_3$ (B)	0.1	>99:<1:0	<1:>99	86:14
3	$RhCl(PPh_3)_3$ (A)	2.0	50:46:4	7:93	84:16
4	$RhCl(PPh_3)_3$ (B)	2.0	>99:<1:0	<1:>99	92:8
5	$RhCl(PPh_3)_3$ (A) + PPh_3	2.0	34:66:<1	20:80	67:33
6	$RhCl(PPh_3)_3$ (B) + PPh_3	2.0	73:27:<1	4:96	92:8
7	$[Rh(COD)Cl]_2$ + $8PPh_3$	2.0	60:40[d]	30:70	64:36

All samples of $RhCl(PPh_3)_3$ were prepared according to the *Inorganic Syntheses* procedures.[47,48] [a] Method A employs catalyst handled under an inert atmosphere at all times; method B uses Wilkinson's catalyst exposed to trace amounts of oxygen. All hydroboration reactions performed via either method were executed under an inert atmosphere, see Experimental Section. [b] Determined by GC. [c] Determined by ^2H NMR; throughout >99:<1 (or vice versa) indicates the minor component was not observed by NMR. [d] Amount of reduction product **19** was not determined.

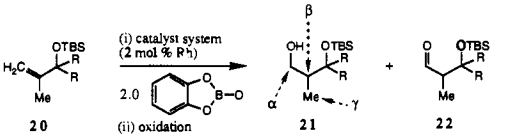
in alcohol **17** increases (entries 3 and 5).

Three questions emerge from these data concerning the origin of (i) α-deuteration, (ii) aldehyde **18**, and (iii) variance in syn:anti selectivity. Evans and Fu proposed an answer to the first issue,[4] i.e., α-deuteration in the hydroboration product **17** is a result of reversible insertion of alkene into a Rh–D bond to give tertiary rhodium alkyl intermediate **II** (Scheme III).

The hypothesis in Scheme III[4] requires 100% diastereoselective β-elimination from the labeled methyl group, CH_2D (as opposed to the diastereotopic methyl CH_3), since deuterium was not found in the CH_3 moiety (Schemes III and IV). It also implies very high diastereofacial selectivity in addition of Rh–D to alkene, as addition to the opposite face would give an alkene–rhodium π-complex with deuterium in the vinylic methyl group. To test this we investigated catalyzed hydroborations of the related achiral substrates **20** (Table VI and Scheme IV). If the tertiary alkyl intermediate **III** is involved, then there can be no diastereoselection between β-elimination from the two *enantiotopic* methyl groups, consequently more deuterium should be observed in the γ-methyl than in the α-methylene. Silyl ether **20a** (R = H, Table VI), however, gave at least three times more deuterium incorporation at the α-position than at the vinylic (γ) methyl group. These observations imply that formation of tertiary alkyl intermediates **III**, followed by β-hydride elimination does not account for most of the α-deuterium incorporation in these substrates. For the more hindered silyl ether **20b** (R = Me), hydroboration was much slower, with less α-deuterium incorporation in the resulting alcohol and more alkene deuteration. The catalyzed hydroborations of **20a** and **20b** gave only deuterated alkane when 0.1 equiv of catecholborane-*d* was used.

Formation of aldehyde in these catalyzed hydroborations is particularly surprising. Aldehyde **18** cannot be formed from alcohol **17** in the oxidation step since **17** is deuterated while **18** is not. Aldehydes arise presumably from oxidation of vinylboronate esters formed via dehydrogenative borylation of silyl ethers **16** and **20**. To investigate this we hydroborated alkene **20a** catalytically and then added 2,3-dimethylbutane-2,3-diol (pinacol) instead of oxidizing. This gave the very stable boronate ester **23**, which could be isolated via flash chromatography.[50] A small

Table VI. Catalyzed Hydroboration of the Silyl Ethers **20** with Catecholborane-*d*

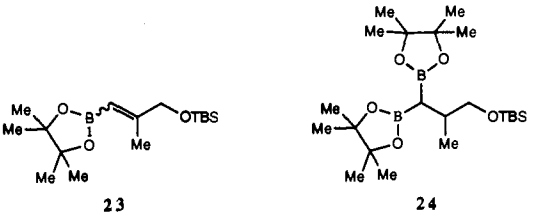


a, R = H; b, R = Me

entry	R	catalyst system[a]	**21**, label distribution α:β:γ	**21**:**22**
1	H	$RhCl(PPh_3)_3$	7:92:<1	83:17
2	H	$RhCl(PPh_3)_3$ + PPh_3	13:83:4	60:40
3	H	$[Rh(COD)Cl]_2$ + $8PPh_3$	16:79:5	60:40
4	Me	$RhCl(PPh_3)_3$	<1:>99:–[b]	93:7
5	Me	$RhCl(PPh_3)_3$ + PPh_3	13:87:–[c]	50:50

[a] Catalyst prepared and manipulated under anaerobic conditions throughout; ratio of hydroboration to deuteration products (addition of D_2 to alkene) not established. [b] Conversion 43% after 18 h. [c] Conversion 5% after 18 h.

amount of a compound tentatively characterized (see Experimental Section) as the bis(boronate ester) **24** was also isolated.



Aldehydes isolated from hydroborations performed with catecholborane-*d* were generally unlabeled. The exception, however, was **22a** from hydroboration of allyl silyl ether **20a**, which contained a small amount of deuterium label at the β-position and a trace at the α-position. β-Deuteration presumably arises from hydroboration of the corresponding vinylboronate ester, i.e., the bishydroboration process that led to bis(boronate ester) **24** in the above experiment.

The experiments outlined above establish that vinylboronate esters are formed in these reactions. Furthermore, other experiments presented in this paper indicate that vinylboronate esters can be hydrogenated under catalyzed hydroboration conditions. We propose that α-deuteration in the catalyzed hydroboration of substrate **16** (and **20**) arises predominantly via addition of D_2 (or HD) to the vinylboronate ester **IV** (Scheme V). This would also explain the absence of deuterium label in the γ-methyl. Hydroboration product also can be formed via direct catalyzed hydroboration according to the mechanism previously outlined in Scheme I, and the relative importance of each of these reaction pathways varies with conditions. This accounts for the variable syn:anti diastereoselectivities in this reaction since each mechanism presumably has a different diastereofacial bias.[51] The decrease in diastereoselectivity cannot be attributed to BH_3-derived products, since these were not detected by ^{11}B NMR.

Rapid insertion/elimination relative to Rh–C bond rotation in the putative intermediates **II** (for **16**) or **III** (for **20**) could account for the higher degree of deuterium incorporation in the α-position than in the vinylic (γ) methyl group of alcohol **17** (or **21**). In this case aldehyde and α-deuterated products presumably would arise from unrelated processes. However, we have never observed substantial α-deuteration without aldehyde formation, and we believe this correlation is unlikely to be coincidental.

An attractive rationale for the formation of vinylboronate esters in catalyzed hydroborations involves insertion of alkenes into rhodium–boron bonds, rather than Rh–H bonds (Scheme V).

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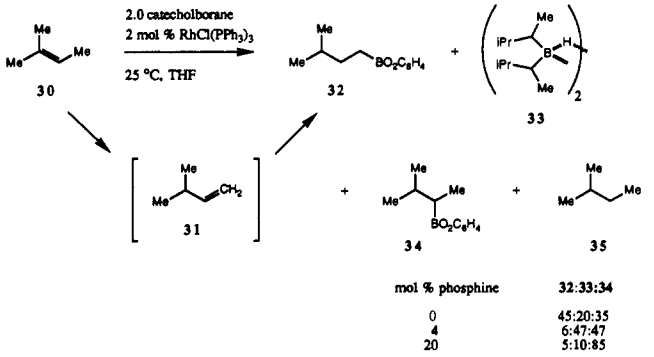
(51) We have been unable to determine if HD, D_2, or a mixture of both is added to the alkene; certainly there is evidence for some HD addition, but at present we are unable to quantify this.

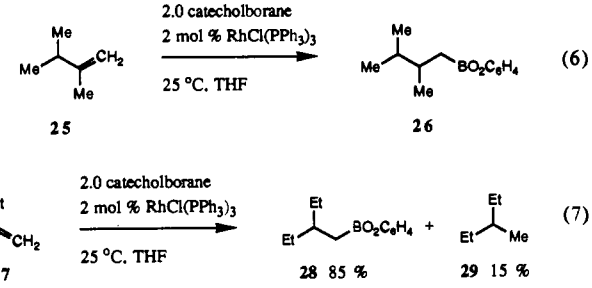
Scheme VI. Catalyzed Hydroborations of 2-Methylbut-2-ene (30)



β-Hydride elimination from the resulting tertiary alkyl-intermediate could give the observed vinylboronate ester. Allylboronate esters were not observed; hence we assume that either these are rapidly isomerized to their vinyl isomers or β-hydride elimination from the boron-substituted carbon is greatly favored. In fact, recently we observed selective activation of C–H on carbons α to boron bonds using rhodium–, iridium–, and ruthenium–phosphine complexes.[36] An alternative mechanism based on direct vinylic or allylic C–H bond activation[52-59] prior to B–C bond formation cannot be excluded. This would involve rhodium(V) intermediates or some other B–H activation process (e.g., σ-bond metathesis), and we consider these options to be less likely.

Catalytic formation of vinylboranes from reactions of alkenes with pentaborane and borazine has been observed previously by Sneddon.[60,61] More recently, vinylboronate esters have been obtained with comparable amounts of hydrogenation products from reactions of alkenes with boron hydrides in the presence of rhodium catalysts.[62] Dehydrogenative borylation of alkenes is analogous to production of vinylsilanes via dehydrogenative silylation of alkenes.[63-70] The mechanistic origin of the trans addition of silanes to alkynes is also thought to involve insertion of the unsaturated organic fragment into the M–Si bond in preference to the M–H bond.[71]

Catalyzed Hydroboration of 2,3-Dimethylbut-1-ene (25) and 2-Ethylbut-1-ene (27). Catalyzed hydroborations of two other 1,1-disubstituted alkenes were investigated to test the scope of aldehyde formation and reduction in catalyzed hydroborations of similar substrates. Alkene **25** gave primary boronate ester **26** in high yield, whereas ca. 15% hydrogenation was observed in the reaction of 2-ethylbut-1-ene (**27**) (eqs 6, 7). Addition of 2 equiv



of triphenylphosphine to the catalyst system retarded these hydroborations and gave more $B_2(O_2C_6H_4)_3$ and $H_3B{\cdot}PPh_3$ without influencing the product distribution. These reactions were followed by multinuclear NMR without isolation of the products, and vinylboronate esters were not observed in either reaction.

Catalyzed Hydroboration of the Trisubstituted Alkene 2-Methylbut-2-ene (30). Hydroboration of this substrate is very slow. Upon completion of the reaction (3 days), three major products were formed. Direct hydroboration of **30** afforded secondary boronate ester **34**, while addition of catecholborane to the isomerized intermediate **31** gave terminal boronate ester **32**. Only trace amounts of hydrogenation product **35** were observed (Scheme VI). Remarkably, significant amounts of disiamylborane (**33**) were formed via addition of BH_3 (from degradation of catecholborane) to substrate **30**.

Added triphenylphosphine had a profound effect on these reactions. Hydroboration of alkene **30** gave less isomerization when catalyzed by $RhCl(PPh_3)_3/2\ PPh_3$, and disiamylborane (**33**) was the major product. A high yield (>85%) of the desired boronate ester **34** resulted when 10 equiv of PPh_3 was added to the catalyst.

These results illustrate the importance of phosphine to rhodium ratios in catalyzed hydroborations for synthetic purposes. Isomerization predominated without added phosphine; 2 equiv of added phosphine suppressed isomerization as the relative amounts of products derived from BH_3 increased. Most of the BH_3 is trapped when 10 equiv of triphenylphosphine was used, and the desired hydroboration product was produced in high yield.

Conclusion

The results described herein underline the complexity of the Wilkinson's catalyst/catecholborane hydroboration system; several rhodium-containing products are formed and appreciable degradation of catecholborane is observed. Furthermore, multinuclear NMR investigations reveal that *alkylboranes* (from addition of 'BH_3') sometimes can be formed in addition to alkylboronate esters in catalyzed hydroborations; this was not apparent in previous work in which intermediate organoboron compounds were oxidized to alcohols before characterization.

Deuterium labeling studies can provide useful information concerning the mechanism of catalyzed hydroborations, but reliable conclusions can be obtained only if these results are supported by other data, notably product distributions. Even then considerable care must be taken; hydroboration products can form via different mechanisms, and deuterium label can be delivered by a number of pathways and rhodium–deuteride species. Therefore label distributions in the products does not necessarily provide information about individual steps in the mechanism(s) of catalyzed hydroboration. Catalyst composition is crucial in promoted hydroboration reactions, and addition of excess phosphine ligand can have a profound effect on product and label distribution, particularly for sterically hindered (slow reacting) alkenes.

Formation of vinylboronate esters in the catalyzed hydroboration of the unsaturated allylic silyl ethers **16** and **20** suggests that insertion of alkenes into the rhodium–boron bond is a viable alternative to insertion into rhodium hydride. Rhodium-catalyzed deuteration of these vinylboronate esters in situ offers an alternative explanation for α-deuterium incorporation in the resulting al-

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kylboronate esters. It is possible that insertion of some alkenes into the Rh–B bond may proceed at rates comparable to, or even greater than, insertion into the Rh–H bond. This is an important corollary to the accepted mechanism of catalyzed hydroboration.

Cleaner systems for catalyzed hydroborations are required if optimum chemo-, regio-, and stereoselectivities are to be obtained in organic syntheses. This could be achieved by using more stable boron hydrides and/or alternative catalysts.

Experimental Section

General Procedures. High-field NMR spectra were recorded on Bruker AF300 (^{1}H at 300 MHz, ^{13}C at 75.4 MHz, ^{11}B at 96.3 MHz), Bruker AC250 (^{1}H at 250 MHz, ^{13}C at 62.9 MHz), General Electric QM-300 (^{1}H at 300 MHz, ^{13}C at 75.4 MHz, ^{31}P at 121 MHz), and Nicolet NMC (^{11}B at 96 MHz) instruments. ^{1}H chemical shifts are reported in δ relative to external TMS and were referenced to residual protons in THF-d_8, and ^{13}C chemical shifts are reported in ppm relative to external TMS using THF-d_8 (25.3) or CD_2Cl_2 (53.8) as an internal standard. For experiments using $CDCl_3$ as solvent. ^{1}H chemical shifts are reported in δ relative to $CHCl_3$ (7.25 ppm) as an internal standard, and ^{13}C chemical shifts are reported in ppm relative to $CDCl_3$ (77.1 ppm) as an internal reference. ^{2}H NMR spectra were recorded on a Bruker AMX-500 at 76.7 MHz with $CDCl_3$ as an internal reference. Multiplicities in ^{1}H NMR are reported as (br) broad, (ov) overlapping, (s) singlet, (d) doublet, (t) triplet, (q) quartet, and (m) multiplet. The carbon multiplicities are listed as (C) quaternary, (CH) methine, (CH_2) methylene, and (CH_3) methyl. ^{11}B and ^{31}P chemical shifts are reported in ppm relative to the external standards $F_3B{\cdot}OEt_2$ and 85% H_3PO_4, respectively. Gas chromatography (GC) was performed on a Shimadzu GC-9A interfaced with an Apple Macintosh IIsi using a 50-m (5% methylphenylsilicone, 0.25 mm i.d. 0.25-μm film thickness) fused silica capillary column (Quadrex 007-2-50-0.25 F); figures obtained for crude reaction mixtures were calibrated by injection of stock solutions containing known amounts of the different products. Thin layer chromatography was performed on silica gel 60 F_{254} plates from Whatman. Flash chromatography was performed on SP Silica Gel 60 (230–600-mesh ASTM). Toluene, THF, diethyl ether (Et_2O), and benzene were distilled immediately before use from sodium benzophenone ketyl, and methanol was distilled from magnesium methoxide. Wilkinson's catalyst was prepared as described in *Inorganic Syntheses*.[47,48] The ethanol used was purged with nitrogen for 25 min and then degassed using three freeze/thaw cycles before use. After filtration under argon the catalyst was carefully washed with distilled Et_2O and stored at −25 °C under argon. The catalyst precursors $[Rh(\mu\text{-}Cl)(COD)]_2$[72] and $RhClO_2(PPh_3)_3$[39] were synthesized according to literature procedures. Trideuterioborane was purchased from Cambridge Isotope Laboratories, and deuteriocatecholborane ($DBO_2C_6H_4$) was prepared according to literature procedures[73,74] and distilled under reduced pressure before use. Alkenes were purchased from commercial suppliers and used as received. Organic solutions were dried over anhydrous $MgSO_4$.

Typical NMR Reaction of Catecholborane with $RhCl(PPh_3)_3$. A solution of catecholborane (5 mg, 0.04 mmol) in 1 mL of CD_2Cl_2 was added dropwise to a solution of $RhCl(PPh_3)_3$ (**1**) (35 mg, 0.04 mmol) in 1 mL of CD_2Cl_2. The resulting mixture was characterized spectroscopically by ^{1}H and ^{31}P NMR. Selected NMR spectroscopic data (for B/Rh = 1:1) are given. ^{1}H NMR: δ −17.37 (br, 1 H), −9.81 (br d, $^2J_{HP}$ = 146 Hz, 1 H), $[RhH_2Cl(PPh_3)_3]$, (**3**); −14.96 (d t, J_{HRh} = 27 Hz, $^2J_{HP}$ = 14 Hz, 1 H), $[RhHCl(BO_2C_6H_4)(PPh_3)_2]$, (**2**): 4.14 (br, 3 H), $[H_3B{\cdot}PPh_3]$. ^{31}P{^{1}H} NMR: −6.3 (br), $[PPh_3]$, 22 (br, 1 P), 40.1 (d, 2 P, J_{PRh} = 114 Hz), (**3**): 22 (br), $[H_3B{\cdot}PPh_3]$; 31.6 (d, J_{PRh} = 114 Hz), $[RhCl(BO_2C_6H_4)_2(PPh_3)_2]$, (**4**); 33.1 (d d, 2 P, J_{PRh} = 143, $^2J_{PP}$ = 39 Hz), 49.6 (d t, 1 P, J_{PRh} = 191 Hz), (**1**); 39.9 (d, J_{PRh} = 117 Hz), (**2**); 53.3 ppm (d, J_{PRh} = 196 Hz). $[[Rh(\mu\text{-}Cl)(PPh_3)_2]_2]$. (**6**). ^{11}B{^{1}H} NMR: −38.3 (br d, J_{BP} = 46 Hz), $[H_3B{\cdot}PPh_3]$; 18.4 (br), $[B_2(O_2C_6H_4)_3]$; 20.9 (br, minor): 35.8 ppm (br), (**2**).

Reactions of $[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$ (8) with Catecholborane. Preparation of $RhHCl(BO_2C_6H_4)(PPh_3)_2$ (2) and $RhCl(BO_2C_6H_4)_2(PPh_3)_2$ (4). A solution of $HBO_2C_6H_4$ (71 mg, 0.6 mmol) in 2 mL of CH_2Cl_2 was added to a suspension of **8** (414 mg, 0.3 mmol) in 8 mL of CH_2Cl_2. After 1 h, the clear yellow solution was diluted with 30 mL of diethyl ether and cooled at −20 °C for 20 h. The resulting cream-colored crystals were washed with 5 mL of diethyl ether and 5 mL of hexane and dried in vacuo to yield 390 mg of **2** (78%).

The following procedure was used to isolate **4**. A solution of $HBO_2C_6H_4$ (1.8 g, 15 mmol) in 2 mL of CH_2Cl_2 was added to a suspension of **8** (660 mg, 0.5 mmol) in 10 mL of CH_2Cl_2. After 4 days the solvent was removed in vacuo and the solid residue was triturated with 20 mL of diethyl ether. The resulting colorless solid was collected by filtration, washed with 3 × 10 mL of diethyl ether, and dried in vacuo to yield 660 mg of **4**. Slow evaporation of the brown-orange filtrate gave a second crop of 80 mg (tan crystals); the total yield of **4** was 740 mg (82%). ^{1}H NMR (CD_2Cl_2): δ 7.71 (m, 12 H, ortho of PPh_3). 7.31 (t, 7 Hz, 6 H, para of PPh_3), 7.26 (m, 12 H, meta of PPh_3), 6.78, 6.69 (m, 4 H. $BO_2C_6H_4$). ^{11}B NMR: 38.2 ppm (v br).

NMR Reaction of $RhHCl(BO_2C_6H_4)(PPh_3)_2$ (2) with PPh_3. A solution of PPh_3 (26 mg, 0.1 mmol) in 0.5 mL of THF-d_8 was added to a solution of **2** (78 mg, 0.1 mmol) in 0.5 mL of THF-d_8, and the reaction was monitored by multinuclear NMR spectroscopy. After 4 h the ratio of **1**:**2**:**3**:**4**:PPh_3 was ca. 5:4:3:1:2 and $B_2(O_2C_6H_4)_3$ was observed by ^{11}B NMR.

NMR Reaction of Catecholborane with $RhCl(PPh_3)_3$ under Catalytic Conditions. A solution of catecholborane (360 mg, 3.0 mmol) in 2 mL of THF-d_8 was added via syringe to a cold (−78 °C) solution of **1** (40 mg, 0.04 mmol) and oct-1-ene (330 mg, 3 mmol) in 3 mL of THF-d_8 in a 10-mm NMR tube. The sample was placed in the −40 °C NMR probe, and the ^{31}P NMR spectrum was recorded. The ratio of **2**:PPh_3:$H_3B{\cdot}PPh_3$ was 12:16:10:1. Once the solution warmed to 25 °C, $H_3B{\cdot}PPh_3$ increased at the expense of free PPh_3, and the ^{11}B NMR spectrum contained minor resonances at 18.1 and −38 ppm due to $B_2(O_2C_6H_4)_3$ and $H_3B{\cdot}PPh_3$ and one major resonance at 35.0 ppm due to $C_8H_{17}BO_2C_6H_4$.

NMR Reactions of Catecholborane with $[Rh(\mu\text{-}Cl)(COD)]_2$/$PPh_3$. Additions of 1 (34 mg, 0.14 mmol), 2, and 3 equiv of PPh_3/Rh to $[Rh(\mu\text{-}Cl)(COD)]_2$ (**6**) (32 mg, 0.07 mmol) at 25 °C in 3 mL of THF-d_8 in 10-mm NMR tubes were monitored at −40 °C by ^{31}P NMR. With a P/Rh ratio of 1, a doublet at 32.6 ppm (J_{PRh} = 152 Hz) was observed due to $RhCl(COD)(PPh_3)$ (**7**). Resonances due to **7** and PPh_3 were broadened due to mutual intermolecular exchange for P/Rh ratios of 2 and 3, and a small amount of **1** was detected in the latter. Subsequent (ca. 40 min later) addition of catecholborane (467 mg, 3.9 mmol) to these samples at 25 °C was monitored at −80 °C by ^{31}P NMR. In addition to $H_3B{\cdot}PPh_3$, **2**, and **3**, a number of doublet resonances characteristic of Rh(III) phosphine complexes were observed between 30 and 60 ppm. Once the samples were warmed to 25 °C, the ^{11}B NMR spectra indicated $B_2(O_2C_6H_4)_3$, $H_3B{\cdot}PPh_3$, and a sharp resonance at 14.3 due to the $[B(O_2C_6H_4)_2]^-$ anion.

In another experiment, the reaction of **6** (23 mg, 0.05 mmol) with 4 equiv of PPh_3/Rh (105 mg, 0.4 mmol) in THF-d_8 was monitored by ^{31}P NMR. After 4.5 h ca. 70% of **7** was converted to **1**. Solutions of **6** containing 4 equiv of PPh_3/Rh prepared as above were allowed to mix for 1 min and 40 min prior to addition of 30 equiv of catecholborane/Rh (360 mg, 3 mmol), and the resulting solutions were monitored by ^{31}P NMR. Although the predominant P-containing species was $H_3B{\cdot}PPh_3$ in both cases, the sample with minimal mixing time contained a number of doublet resonances characteristic of Rh(III) phosphine complexes and three triplet of multiplet resonances at 85.8 (J_{PRh} = 87 Hz), 83.8 (J_{PRh} = 85 Hz), and 81.8 ppm (J_{PRh} = 84 Hz).

Molecular Structure Determinations. Crystals of **3** and **5** suitable for X-ray diffraction studies were obtained by recrystallization from THF at −30 °C. A summary of the crystallographic results is presented in Table I. Both sets of data were collected at low temperatures on an Enraf-Nonius CAD4 diffractometer using graphite-filtered Mo Kα radiation (λ = 0.710 69 Å) and ω scan methods. The data were reduced in the usual fashion for Lorentz polarization and corrected for 3% (**3**) and 11% (**5**) decreases in intensity vs the standard reflections. Azimuthal scans also showed some variation in intensity, and empirical corrections were made for **5**. The data set for **5** was also corrected for absorption via the DIFABS method.[75] The solution and refinement of the structures were performed on a VAX/IBM cluster system using a local program set. For **3**, the structure was solved by direct methods (SHELXS).[76] For **5**, the heavy atom positions were obtained via automated Patterson analysis and used to phase the reflections for the remaining light atoms by the usual combination of structure factor, Fourier synthesis, and full-matrix least-squares refinement. All refinements were performed using full matrix least squares on F, with anisotropic thermal parameters for all non-hydrogen atoms, and included anomalous dispersion terms[77] for Rh, Cl, and P, as well as idealized hydrogen coordinates as fixed atom

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contributors. The coordinates used were those corresponding to the enantiomorph with the lowest R value. The atomic scattering factors were taken from the tabulations of Cromer and Waber.[78] For **3**, there are two independent molecules and two disordered THF solvent molecules, each on a different center of symmetry in the asymmetric unit. The disordered THF molecules were modeled as C atoms, some with partial occupancies. Although the cell can be transformed into a metric centered monoclinic cell, lack of mirror symmetry in the data implied there is a 0.93/0.07 statistical distribution of the chloride ligand across the Rh-P2-P3-P4 plane. For **5**, the asymmetric unit consists of one molecule of the complex, one THF molecule, and one unidentified molecule of solvent in general positions. The positional parameters of the Rh hydride were refined, but the thermal parameter was not. The electron density in the channels between the molecules of **5** was modeled as disordered unidentified solvent. Tables of bond distances and angles, final position and thermal parameters for the non-hydrogen atoms, general temperature factors, calculated hydrogen atom positions, and structure factor listings are available as supplementary material.

Representative Procedure for Catalyzed Hydroboration: Catalyzed Hydroboration of Phenylethene (10). A Schlenk tube was charged with 9 mg (0.01 mmol, 0.002 equiv) of $RhCl(PPh_3)_3$ in an argon atmosphere. The tube was evacuated/flushed three times with argon and then THF (1 mL) was added, followed by 520 mg (5 mmol) of phenylethene (**10**) in 1 mL of THF. After the burgundy-red solution was stirred for 5 min at 25 °C, 60 mg of $DBO_2C_6H_4$ (0.5 mmol, 0.1 equiv) was added. The color faded to light yellow, and the reaction mixture was stirred for another hour. Ethanol (1 mL) was added, followed by 1.7 mL of a 3 M NaOH solution and 1 mL of 30% H_2O_2 at 0 °C. The mixture was stirred for 6 h at 25 °C, diluted with 50 mL of Et_2O, and washed with a 1 M NaOH solution (30 mL). The aqueous layer was extracted with Et_2O (2 × 50 mL), and the combined organic fractions were washed with 1 M NaOH (50 mL), water (50 mL), and saturated NaCl solution (50 mL). The organic layer was dried, and the crude product was obtained by evaporating the solvent under reduced pressure. A ^2H NMR spectrum was recorded for the crude product; 1-phenylethanol (**11**) was the only hydroboration product detected, together with a trace amount of deuterated ethylbenzene. This was confirmed by capillary GC of the trimethylsilyl derivative.

Catalyzed Hydroboration of Phenylethene (10) with $RhCl(PPh_3)_3$ in the Presence of O_2. A Schlenk tube charged with 18.4 mg (0.02 mmol) of **1** was evacuated/flushed with argon three times and then 2 mL of THF was added, followed by 104 mg (1 mmol) of phenylethene (**10**). Oxygen (1 mL) was introduced into the atmosphere above the solution with a syringe, the solution turned orange-brown, and the solution was stirred for 10 min prior to the addition of 240 mg (2 mmol) of catecholborane at 25 °C. After being stirred for 1 h, the reaction mixture was oxidized, followed by workup as described previously. The alcohols present in the crude reaction mixture were transformed into the trimethylsilyl derivatives, and analysis by capillary GC gave **11** and **12** in a ratio of 60:40.

Hydroboration of Phenylethene (10) Catalyzed by $RhCl(O_2)(PPh_3)_3$ (9). The oxidation product **9** was prepared as described by Gahan and co-workers.[39] The light brown complex was isolated under argon; the ^{31}P NMR spectrum obtained was identical to that reported previously.[39] A Schlenk tube was charged with 0.02 mmol of complex **9** and evacuated/flushed with argon. A solution of 240 mg (2 mmol) of catecholborane and 104 mg (1 mmol) of phenylethene in 2 mL of THF was added at 25 °C. The reaction mixture was stirred for 1 h and oxidized, and then the crude product was isolated and analyzed by capillary GC (trimethylsilyl derivatives), showing a ratio of 99:1 for **11**:**12**. In another experiment 2 mL of THF was added to a Schlenk tube containing 0.02 mmol of **9**, and the solution was stirred for 1 h at 25 °C prior to addition of 1 mmol of phenylethene and 2 mmol of catecholborane. The reaction mixture was stirred for 1 h and oxidized, and the crude product was analyzed, providing a ratio of 14:86 for **11**:**12**.

Catalyzed Hydroboration of Phenylethyne. The general procedure as described for the catalyzed hydroboration of phenylethene (**10**) was followed. After 1–1.5 h, part of the reaction mixture was transferred and oxidized, while the remaining solution was stirred for an additional 11–13 h prior to oxidation (see Table IV). The product distributions were determined by ^1H NMR.

Catalyzed Hydroboration of 1-Hexyne Monitored by ^{11}B NMR. A Schlenk tube was charged with 0.02 mmol of $RhCl(PPh_3)_3$ in an argon atmosphere. The tube was evacuated/flushed with argon three times, and 1.0 mL of THF was added followed by 0.1 mL of degassed benzene-d_6. 1-Hexyne (1.0 mmol) was added, followed by 2 mmol of catecholborane. An NMR sample was prepared under argon using a tube equipped with a screw cap with septum and containing a sealed capillary with $F_3B{\cdot}Et_2O$ in benzene-d_6. The ^{11}B NMR spectrum of this sample was recorded at 15-min intervals and compared with spectra from authentic samples (prepared according to literature procedures[79]) of 2-(1-hexenyl)-1,3,2-benzodioxaborole (^{11}B at 31 ppm), 2-(1-hexyl)-1,3,2-benzodioxaborole (^{11}B at 35.5 ppm), and catecholborane (^{11}B at 25.5 ppm). An additional 0.5 mmol of catecholborane was added to the reaction mixture after all the catecholborane had disappeared, and further ^{11}B NMR spectra recorded at 15-min intervals showed evidence for further reduction of the vinylboronate ester. Oxidation of the reaction mixture afforded 1-hexanol and hexanal.

Rhodium-Catalyzed Hydroboration of 2-(1-Hexenyl)-1,3,2-benzodioxaborole with Catecholborane. 2-(1-Hexenyl)-1,3,2-benzodioxaborole was prepared as described by Brown[79] from 1-hexyne and catecholborane. The product was distilled (91 °C, 0.35 Torr), and 1 mmol was added to a mixture of 0.02 mmol of $RhCl(PPh_3)_3$ and 2 mmol of catecholborane. After 4 h, 1.0 mL of ethanol was added to the reaction mixture at 0 °C, followed by 2.0 mL of saturated $NaHCO_3$ solution and 1.0 mL of 30% H_2O_2 solution. The solution was stirred for 4 h, diluted with diethyl ether, and washed with 1.0 M NaOH. The mixture was analyzed by GC after drying and partial evaporation of the solvent, and about 25% 1-hexanol was detected. A ^{13}C NMR spectrum of the crude product shows hexanal, 1-hexanol, and polymerization products. Repeating the procedure with $[Rh(\mu\text{-}Cl)(COD)]_2/8PPh_3$ gave similar results.

Catalyzed Hydroborations of 2-Methyl-3-((*tert*-butyldimethylsilyl)oxy)but-1-ene (16). The general procedure for catalyzed hydroboration was followed with either 0.1 or 2 equiv of catecholborane-*d*. Different results were obtained depending on whether the catalyst was rigorously handled in an inert atmosphere (method A) or exposed to trace amounts of oxygen (method B), as indicated in Table V. After 12 h, the reaction mixture was oxidized using 2 mL of a 2.0 M pH 7 phosphate buffer and 1 mL of 30% H_2O_2. A ^2H NMR spectrum (Table III) was obtained for the crude product, and the reaction products were analyzed by capillary GC. The individual components were then separated by flash chromatography.[80] **2-Methyl-3-((*tert*-butyldimethylsilyl)oxy)but-1-ene (16).** ^1H NMR (300 MHz, $CDCl_3$): δ 0.02 (s, 3 H), 0.04 (s, 3 H), 0.85 (s, 9 H), 1.20 (d, J = 6.3 Hz, 3 H), 1.68 (s, 3 H), 4.19 (q, J = 6.3 Hz, 1 H), 4.69 (m, 1 H), 4.88 (m, 1 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ −5.0 (CH_3), −4.9 (CH_3), 17.6 (CH_3), 18.3 (C), 23.3 ($C(CH_3)_3$), 25.9 (CH_3), 72.4 (CH), 109.1 (CH_2), 149.2 (C). ***syn*-2-Deuterio-2-methyl-3-((*tert*-butyldimethylsilyl)oxy)butan-1-ol (17).** The syn isomer was obtained as the major product of the rhodium-catalyzed hydroboration. TLC: R_f 0.15 (EtOAc/hexane 5:95). ^1H NMR (250 MHz, $CDCl_3$): δ 0.06 (s, 3 H), 0.07 (s, 3 H), 0.75 (s, 3 H), 0.88 (s, 9 H), 1.11 (d, J = 6.4 Hz, 3 H), 3.09 (br s, 1 H), 3.44–3.55 (m, 1 H), 3.66–3.70 (m, 1 H), 3.96 (q, J = 6.4 Hz, 1 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ −5.0 (CH_3), −4.5 (CH_3), 12.3 (CH_3), 17.9 (C), 18.3 (CH_3), 25.8 ($C(CH_3)_3$), 40.9 (t, $^1J_{CD}$ = 18 Hz, CD), 65.6 (CH_2), 72.1 (CH). ***anti*-2-Deuterio-2-methyl-3-((*tert*-butyldimethylsilyl)oxy)butan-1-ol (17).** Analytical data for the anti isomer were obtained from hydroboration of **16** with BD_3, which provides the anti diastereomer as the major product.[27] TLC: R_f 0.15 (EtOAc/hexane 5:95). ^1H NMR (250 MHz, $CDCl_3$): δ 0.06 (s, 3 H), 0.07 (s, 3 H), 0.87 (s, 9 H), 0.94 (s, 3 H), 1.19 (d, J = 6.2 Hz, 3 H), 2.91 (br s, 1 H), 3.46–3.54 (m, 1 H), 3.68–3.80 (m, 1 H), 3.97 (q, J = 6.3 Hz, 1 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ −5.0 (CH_3), −4.6 (CH_3), 14.6 (CH_3), 17.9 (C), 22.1 (CH_3), 25.8 (CH_3), 41.7 (t, $^1J_{CD}$ = 19 Hz, CD), 65.8 (CH_2), 73.9 (CH). **2-Methyl-3-((*tert*-butyldimethylsilyl)oxy)butan-1-al (18).** The compound was obtained as an inseparable mixture of diastereomers. TLC: R_f 0.4 (EtOAc/hexane 5:95). ^1H NMR (250 MHz, $CHCl_3$): δ 0.02 (s, 3 H, $Si(CH_3)_2$), 0.86 (s, 9 H, $C(CH_3)_3$), 1.02 (d, J = 8.4 Hz, 3 H, two overlapping doublets from the two diastereoisomers), 1.13 (d, J = 10.1 Hz, 3 H), 1.16 (d, J = 9.9 Hz, 3 H), 2.38 (m, 1 H), 3.98 (m, 1 H), 4.23 (m, 1 H), 9.74 (d, 2.6 Hz, 1 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ −5.0 (CH_3), −4.2 (CH_3), 8.1 (CH_3), 10.7 (CH_3), 17.9 (C), 21.2 (CH_3), 21.8 (CH_3), 25.7 ($C(CH_3)_3$), 53.4 (CH), 53.7 (CH), 68.2 (CH), 69.9 (CH), 205.1 (CHO). **2-Methyl-3-((*tert*-butyldimethylsilyl)oxy)butane (19).** An authentic sample of the title compound was prepared for calibration purposes from 3-methyl-2-butanol using Corey's silylation procedure.[81] ^1H NMR (300 MHz, $CDCl_3$): δ 0.02 (s, $Si(CH_3)_2$), 0.83–0.91 (m, 15 H), 1.05 (d, J = 6.2 Hz, 3 H), 1.56 (m, 1 H), 3.54 (m, 1 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ −4.7 (CH_3), −4.2 (CH_3), 18.1 (CH_3), 18.2 (C). 18.4 (CH_3),

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26.0 ($C(CH_3)_3$), 35.5 (CH), 73.1 (CH). ^2H NMR for partially deuterated material (76.7 MHz, $CHCl_3$): δ 0.86, 1.56.

Catalyzed Hydroboration of 2-Methyl-3-((*tert*-butyldimethylsilyl)oxy)prop-1-ene (20, R = H). The general procedure as illustrated for catalyzed hydroboration of phenylethene (**10**) was followed, and the reaction mixture was oxidized after being stirred at 25 °C for 12 h. A ^2H NMR spectrum (Table VI) was obtained on the crude product, and reaction products were analyzed by capillary GC. The individual components then were separated by flash chromatography. **2-Methyl-3-((*tert*-butyldimethylsilyl)oxy)prop-1-ene (20, R = H).** ^1H NMR (250 MHz, $CDCl_3$): δ 0.07 (s, 6 H, $Si(CH_3)_2$), 0.92 (s, 9 H, $C(CH_3)_3$), 1.69 (s, 3 H, CH_3), 4.03 (s, 2 H, CH_2OR). 4.80 (s, 1 H), 4.98 (s, 1 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ −5.3 ($Si(CH_3)_2$). 18.5 (C), 19.0 (CH_3), 26.0 ($C(CH_3)_3$), 66.9 (CH_2OR), 109.3 (CH_2), 144.6 (C). **2-Methyl-3-((*tert*-butyldimethylsilyl)oxy)propan-1-ol (21, R = H).** ^1H NMR (300 MHz, $CDCl_3$): δ 0.04 (s, 6 H, $Si(CH_3)_2$), 0.81 (d, J = 6.9 Hz, 3 H, CH_3), 0.87 (s, 9 H, *t*-Bu), 1.89 (m, 1 H), 2.99 (br s, 1 H, OH), 3.60 (m, 4 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ −5.6 ($Si(CH_3)_2$), 13.1 (CH_3), 18.2 (C), 25.9 ($C(CH_3)_3$), 37.1 (CH). 68.1 (CH_2), 68.6 (CH_2). ^2H NMR (76.7 MHz. $CHCl_3$): δ 0.89 (CH_2D), 1.91 (CD), 3.61 (CHDO-H). **2-Methyl-3-((*tert*-butyldimethylsilyl)oxy)propan-1-al (22, R = H).** ^1H NMR (300 MHz, $CDCl_3$): δ 0.04 (s, 6 H. $Si(CH_3)_2$). 0.86 (s, 9 H, $C(CH_3)_3$), 1.07 (d, J = 7.1 Hz, 3 H), 2.51 (m, 1 H), 3.81 (m, 2 H), 9.71 (d, 1.4 Hz). ^{13}C NMR (75.4 MHz. $CDCl_3$): δ −5.5 ($Si(CH_3)_2$). 10.4 (CH_3), 18.3 (C). 25.9 ($C(CH_3)_3$), 48.9 (CH), 63.5 (CH_2), 204.8 (CHO). **2-Methyl-1-((*tert*-butyldimethylsilyl)oxy)propane.** An authentic sample of the title compound was prepared for calibration purposes from 2-methyl-1-propanol using Corey's silylation procedure.[61] ^1H NMR (250 MHz, $CDCl_3$): δ 0.03 (s, 6 H, $Si(CH_3)_2$). 0.86 (m, 15 H), 1.71 (m, 1 H), 3.33 (d, J = 7.8 Hz, 2 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ −5.3 ($Si(CH_3)_2$), 18.5 (C), 19.1 (CH_3), 26.1 ($C(CH_3)_3$), 31.0 (CH), 70.0 (CH_2). ^2H NMR for partially deuterated material (76.7 MHz, $CHCl_3$): δ 0.85, 1.68.

Catalyzed Hydroboration of 2,3-Dimethyl-3-((*tert*-butyldimethylsilyl)oxy)but-1-ene (20, R = Me). The general procedure was followed (see illustrative procedure for catalyzed hydroboration). After 12 h, the reaction mixture was oxidized as described above. A ^2H NMR spectrum (Table VI) was recorded for the crude product. The reaction products were analyzed by GC analysis prior to separation by flash chromatography. **2,3-Dimethyl-3-((*tert*-butyldimethylsilyl)oxy)but-1-ene (20, R = Me).** TLC: R_f 0.85 (hexane). ^1H NMR (250 MHz, $CDCl_3$): δ 0.04 (s, 6 H. $Si(CH_3)_2$). 0.89 (s, 9 H, $C(CH_3)_3$), 1.36 (s, 6 H, CH_3), 1.79 (s, 3 H, CH_3), 4.66 (s, 1 H), 4.94 (s, 1 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ −2.1 ($Si(CH_3)_2$). 18.4 (C), 19.2 (CH_3). 25.9 ($C(CH_3)_3$), 29.6 (CH_3), 75.6 (C), 108.3 (CH_2), 152.6 (C). **2,3-Dimethyl-3-((*tert*-butyldimethylsilyl)oxy)butan-1-ol (21, R = Me).** TLC: R_f 0.15 (EtOAc/hexane 10:90). ^1H NMR (300 MHz, $CDCl_3$): δ 0.13 (s, 6 H, $Si(CH_3)_2$), 0.86 (s, 9 H, $C(CH_3)_3$), 0.92 (d, J = 7.2 Hz, 3 H), 1.22 (s, 3 H), 1.30 (s, 3 H). 1.65 (m, 1 H), 3.12 (br s, 1 H, OH), 3.76 (m, 2 H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ −1.8 ($Si(CH_3)_2$), 13.1 (CH_3), 18.2 (C), 26.0 (C-(CH_3)$_3$), 29.6 (CH_3). 45.7 (CH), 66.1 (CH_2), 78.2 (C). **2,3-Dimethyl-3-((*tert*-butyldimethylsilyl)oxy)butan-1-al (22, R = Me).** R_f 0.35 (EtOAc/hexane 10:90). ^1H NMR (300 MHz, $CDCl_3$): δ 0.10 (s, 6 H. $Si(CH_3)_2$), 0.86 (s, 9 H, $C(CH_3)_3$), 1.06 (d, J = 7.0 Hz, 3 H), 1.24 (s, 3 H), 1.31 (s. 3 H), 2.31 (dq, J = 2.7 Hz, J = 7.0 Hz, 1 H), 9.84 (d, 2.8 Hz, 1 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ −2.4 ($Si(CH_3)_2$). 9.2 (CH_3), 17.8 (C), 25.6 ($C(CH_3)_3$), 27.0 (CH_3), 57.1 (CH), 74.8 (C), 206.1 (CHO).

Catalyzed Hydroboration of 20 (R = H), Followed by Transesterification of the Intermediate Boronate Ester. The general procedure as illustrated for catalyzed hydroboration of phenylethene (**10**) was followed, and upon completion of the reaction (GC), 354 mg (3 mmol, 3 equiv) of pinacol in 2 mL of THF was added. The reaction mixture was stirred for 16 h, and the crude product was subjected to flash chromatography. Elution with 3% EtOAc in hexane gave an inseparable mixture of pinacol (2-methyl-3-((*tert*-butyldimethylsilyl)oxy)-1-propyl)boronate and pinacol (2-methyl-3-((*tert*-butyldimethylsilyl)-oxy)-1-propenyl)boronate (**23**) (R_f 0.5), while **24** was obtained pure (R_f 0.35). **Pinacol (2-Methyl-3-((*tert*-butyldimethylsilyl)oxy)-1-propyl)-boronate.** ^1H NMR (300 MHz, $CDCl_3$): δ 0.01 (s, 6 H), 0.56 (dd, J = 6.7 Hz, J = 15.6 Hz, 2 H), 0.88 (s, 9 H), 0.89 (d, J = 6.7 Hz. 3 H), 1.16 (s. 12 H), 1.78–1.85 (m, 1 H), 3.29 (dd. J = 7.2 Hz, J = 9.6 Hz, 1 H), 3.41 (dd, J = 5.7 Hz. J = 9.6 Hz, 1 H). ^{13}C NMR (62.9, $CDCl_3$): δ −5.2 ($Si(CH_3)_2$), 15.7 (br s, CH_2B), 18.5 (C), 19.1 (CH_3), 24.9 (CH_3), 25.0 (CH_3). 26.1 ($C(CH_3)_3$), 32.3 (CH). 70.1 (CH_2), 82.9 (C). MS (FAB): 315 (M + 1). **Pinacol (2-Methyl-3-((*tert*-butyldimethylsilyl)-oxy)-1-propenyl)boronate (23).** Selected NMR spectroscopic data are given. ^1H NMR (250 MHz, $CDCl_3$): δ 0.03 (s, 6 H), 0.90 (s, 9 H). 1.24 (s, 12 H), 4.02 (s, 2 H), 5.46 (s, 1 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 68.4 (CH_2), 82.6 (C), 109 (br s, CHB), 160.0 (C). **(2-Methyl-3-((*tert*-butyldimethylsilyl)oxy)-1,1-propylidene)bis(pinacol boronate) (24).** ^1H NMR (250 MHz. $CDCl_3$): δ 0.00 (s, $Si(CH_3)_2$, 6 H). 0.66 (d. J = 10.1 Hz, 1 H), 0.86 (s, $C(CH_3)_3$, 9 H), 0.97 (d, J = 6.6 Hz, 3 H), 1.20 (ov s, 24 H), 1.97–2.03 (m, 1 H), 3.21 (ov dd. 1 H), 3.57 (dd, J = 3.9 Hz, J = 9.5 Hz, 1 H). ^{13}C NMR (62.9, $CDCl_3$): δ −5.2 ($Si(CH_3)$), −5.1 ($Si(CH_3)$), 15.1 (br s, CHB_2), 18.4 (C), 19.4 (CH_3), 24.6 (CH_3), 25.0 (CH_3), 26.1 ($C(CH_3)_3$), 33.8 (CH), 69.7 (CH_2). 83.0 (C). MS (FAB): 441 (M + 1).

General Procedure for Direct Observation of Alkene/Alkyne Hydroboration (without Oxidation Workup). All reactions were carried out under an atmosphere of dry nitrogen using a continuous purge glovebox. A solution of catecholborane (250 mg, 2.1 mmol) in 1 mL of THF-d_8 was added dropwise to a mixture of the alkene/alkyne (2.0 mmol) and catalyst (0.04 mmol) in 1 mL of THF-d_8. In some experiments, PPh_3 was added to the catalyst/substrate mixture prior to addition of catecholborane. The resulting solutions were stirred for 30 min and then analyzed by high-field ^1H, ^{13}C, and ^{11}B NMR spectroscopy.

Catalytic Hydroboration of 2,3-Methylbut-1-ene (25): Synthesis of 26. ^1H NMR (THF-d_8): δ 0.89 (d. J = 7 Hz, 3 H), 0.92 (d, J = 7 Hz, 3 H), 0.98 (d. J = 7 Hz, 3 H), 1.09–1.18 (ov m, 1 H), 1.35 (d d, J = 16, 7 Hz, 1 H), 1.59 (ov m, J = 7 Hz, 1 H), 1.85 (ov m, 1 H), 7.05 (ov m, 2 H), 7.17 (ov m, 2 H). ^{13}C NMR: 17.1 (br, BCH_2), 19.7 (2 CH_3), 20.8 (CH_3), 35.4 (CH), 36.5 (CH), 113.3 (CH), 123.6 (CH), 149.7 (C) $^{11}B\{^1H\}$ NMR: 35.8 (br).

Catalytic Hydroboration of 2-Ethylbut-1-ene (27): Synthesis of 28. ^1H NMR (THF-d_8): δ 0.91 (t. J = 7 Hz, 6 H), 1.28 (d, J = 7 Hz, 2 H), 1.29–1.54 (ov m, 4 H), 1.54–1.65 (ov m, J = 7 Hz, 1 H), 7.08 (ov m, 2 H), 7.22 (ov m. 2 H). ^{13}C NMR: 12.0 (2 CH_3), 16.4 (br, BCH_2), 29.7 (2 CH_2), 38.7 (CH). 113.0 (CH), 123.4 (CH), 149.6 (C). $^{11}B\{^1H\}$ NMR: 35.2 (br).

Catalytic Hydroboration of 2-Methylbut-2-ene (30): Synthesis of 34. The reaction of **30** (140 mg, 2 mmol) with catecholborane (264 mg, 2.2 mmol) in THF-d_8 in the presence of **1** (37 mg, 0.04 mmol) and 10 equiv of PPh_3 (105 mg, 0.4 mmol) was monitored by ^1H, ^{13}C, and ^{11}B NMR spectroscopy. Upon completion of the reaction, compound **34** was the major product, along with small amounts of compounds **32** and **33** and ca. 5% of the hydrogenation product **35**. Authentic samples of **32**, **33**, and **35** were used to confirm the identity of these compounds in THF. ^1H NMR: δ 0.99 (d, J = 7 Hz, 3 H), 1.02 (d, J = 7 Hz. 3 H). 1.18 (d. J = 7 Hz, 3 H), 1.45 (m. 1 H), 1.93 (m, 1 H), 7.02 (m, 2 H), 7.20 (ov m, 2 H). ^{13}C NMR: 13.1 (CH_3), 22.1 (2 CH_3), 25.3 (br BCH), 31.6 (CH), 112.8 (CH), 123.3 (CH), 149.5 (C). $^{11}B\{^1H\}$ NMR: 35.3 (br).

Catalytic Hydroboration of 3-Methylbut-1-ene (31): Synthesis of 32. ^1H NMR (THF-d_8): δ 0.94 (d. J = 7 Hz, 6 H), 1.26 (t, J = 7 Hz, 2 H), 1.55 (ov m, 3 H), 6.96 (ov m, 2 H), 7.17 (ov m, 2 H). ^{13}C NMR: 9.3 (br. BCH_2). 22.9 (2 CH_3), 31.1 (CH), 33.8 (CH_2), 113.0 (CH), 123.3 (CH), 149.6 (C). $^{11}B\{^1H\}$ NMR: 35.1 (br).

Acknowledgment. Professor D. A. Evans (Harvard) informed us that Wilkinson's catalyst that has been exposed to oxygen and that which was prepared under anaerobic conditions behave differently in catalyzed hydroborations; it was that communication that motivated us to investigate deuterium labeling studies presented herein. We thank Dr. A. Kook (Rice), Nancy J. Herling, Elwood A. Conaway, and Will J. Marshall (Du Pont) for expert technical assistance. We also thank Dr. Mark J. Burk (Du Pont) for many valuable discussions. T.B.M. acknowledges support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Natural Sciences and Engineering Research Council of Canada; K.B. acknowledges support from The National Science Foundation (CHE-8906969) and The Robert A. Welch Foundation. K.B. is a recipient of an NIH Career Development Award (1992–7).

Supplementary Material Available: Tables of bond distances and angles, final position and thermal parameters for the nonhydrogen atoms, general temperature factors, and calculated hydrogen atom position (32 pages); observed and calculated structure factor listings (32 pages). Ordering information is given on any current masthead page.