cyclohexene (42.5 mg, 0.20 mmol), 4-[*N*-(phenylmethyl)carbamoyl]-cyclohexene (43.1 mg, 0.20 mmol), pentadecane (42.5 mg, 0.20 mmol), and $[Ir(cod)(PCy_3)(py)]PF_6$ (8.0 mg, 0.01 mmol) in 1.0 mL of $ClCH_2CH_2Cl$. The resulting homogeneous, pale yellow solution was stirred at 20 °C for 1.8 h and then subjected to a neutral oxidative workup. An aliquot was analyzed by GLC, which showed 93% recovered 4-[(*tert*-butyldimethylsilyl)oxy]cyclohexene and 3% of the derived alcohols and 36% recovered 4-[*N*-(phenylmethyl)carbamoyl]cyclohexene and 51% of the derived alcohol.

Solvent Effect on Stereoselectivity (Table X). CB (120 mg, 1.00 mmol) was added to a mixture of 1-(3-cyclohexenylcarbonyl)pyrrolidine (90 mg, 0.50 mmol) and catalyst (0.02 mmol) in 2.0 mL of solvent. The resulting homogeneous, pale yellow solution was stirred at 20 °C for 15 h and then subjected to a neutral oxidative workup. The unpurified reaction product was acetylated, and an aliquot was analyzed by GLC.

Hydroboration of *N*-(Phenylmethyl)-4-pentenamide. CB (192 mg, 1.60 mmol) was added to a solution of *N*-(phenylmethyl)-4-pentenamide (76 mg, 0.40 mmol) in 2.0 mL of $ClCH_2CH_2Cl$. The resulting mixture was stirred at 20 °C for 30 min and then cooled to 0 °C and stirred under vacuum for 25 min.[49] The reaction was then warmed to 20 °C, and $[Ir(cod)(PCy_3)(py)]PF_6$ (16.0 mg, 0.02 mmol) was added. The mixture immediately turned homogeneous, almost colorless. The solution was stirred at 20 °C for 40 min and then subjected to a neutral oxidative workup. The oxidized mixture was extracted (EtOAc/1 N NaOH), dried over $MgSO_4$, filtered, and concentrated. An aliquot was analyzed by GLC, which showed a 3:1 (primary:secondary) mixture of alcohols (compared with authentic products prepared independently by opening the relevant lactones with benzylamine). The alcohol products were isolated by flash chromatography, affording 17.2 mg (21%) of the secondary alcohol and 47.2 mg (57%) of the primary alcohol.

4-Hydroxy-*N*-(phenylmethyl)pentanamide: R_f = 0.20 (EtOAc); IR (neat) 3300, 2970, 2930, 1650, 1550, 1455, 1430, 1130, 1080 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25-7.40 (m, 5 H, aromatic H), 6.09 (br s, 1 H, N*H*), 4.42 (d, 2 H, J = 5.7 Hz, CH_2Ph), 3.84 (m, 1 H, C*H*OH), 2.38 (dt, 2 H, J = 2.3, 7.0 Hz, CH_2CO), 1.84 (m, 1 H, C*H*HCHOH), 1.71 (m, 1 H, CH*H*CHOH), 1.20 (d, 3 H, J = 6.2 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.34, 138.20, 128.72, 127.79, 127.52, 67.52, 43.76, 34.30, 33.18, 23.66; HRMS m/z calcd for $C_{12}H_{18}N_1O_2$ $(M + H)^+$ 208.1338, found 208.1346.

5-Hydroxy-*N*-(phenylmethyl)pentanamide: R_f = 0.15 (EtOAc); IR ($CHCl_3$) 3450, 3340, 3010, 2940, 1665, 1515, 1455, 1235 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.25-7.40 (m, 5 H, aromatic H), 5.77 (br s, 1 H, N*H*), 4.46 (d, 2 H, J = 5.7 Hz, CH_2Ph), 3.66 (q, 2 H, J = 5.8 Hz, CH_2OH), 2.28 (t, 2 H, J = 7.1 Hz, CH_2CO), 1.55-1.85 (m, 5 H, $CH_2CH_2CH_2OH$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.12, 138.35, 128.61, 127.69, 127.39, 61.89, 43.54, 35.97, 31.95, 21.79. Anal. Calcd for $C_{12}H_{17}N_1O_2$: C, 69.54; H, 8.27. Found: C, 69.40; H, 8.25.

Acknowledgment. Support has been provided by the National Institutes of Health and the National Science Foundation. The NIH BRS Shared Instrumentation Grant Program (1 S10 RR01748-01A1) is acknowledged for providing NMR facilities. The authors wish to express their gratitude to Dr. Benjamin A. Anderson for his editorial efforts.

Supplementary Material Available: Details of selected experimental procedures and stereochemical proofs of the products derived from reactions illustrated in eq 9 and Table IX (4 pages). Ordering information is given on any current masthead page.

(49) It is necessary to remove H_2 from the reaction system prior to addition of the catalyst in order to minimize substrate hydrogenation.

Mechanistic Study of the Rhodium(I)-Catalyzed Hydroboration Reaction

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Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. *Received December 13, 1991*

Abstract: The objective of this study has been to elucidate the mechanism of the rhodium(I)-catalyzed hydroboration process. Evidence that the reaction proceeds through a multistep pathway analogous to that of transition metal catalyzed olefin hydrogenation is presented. Deuterium labeling experiments reveal reversible elementary steps in the catalytic cycle; the level of reversibility is found to be substrate-dependent. Catalyst contamination through contact with adventitious oxidants has a pronounced effect on the reaction and appears to be the source of reported disparities involving product regioselection and deuterium labeling experiments.

In the preceding study,[2] the scope and synthetic applications of the transition metal catalyzed hydroboration reaction were presented. The objective of this companion investigation is to reveal some of the important mechanistic details of this process.

Fundamental mechanistic differences between the catalyzed hydroboration reaction and its uncatalyzed counterpart are manifested in the complementary chemo- and stereoselectivity of the two processes.[3] In their original report, Männig and Nöth suggested a mechanism for $Rh(PPh_3)_3Cl$-catalyzed hydroboration (Figure 1)[4] which is analogous to that proposed for other, more thoroughly investigated rhodium-catalyzed olefin addition reactions such as hydrogenation, hydrosilylation, and hydroformylation.[5] Support for this pathway was provided by their observation that adduct **1**, first isolated by Kono and Ito,[6] reacts stoichiometrically with olefins to afford hydroboration products.[4]

While significant effort has been focused on the catalyzed hydroboration reaction as a synthetic method,[2,3] few investigations have probed the mechanistic details of this process.[3,7-9] As a result, efforts to rationalize the unique behavior of the catalyzed process have been framed in the absence of a fundamental understanding of the elementary steps in the catalytic cycle. For

(1) (a) National Science Foundation Predoctoral Fellow. (b) National Institutes of Health Postdoctoral Fellow.

(2) Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.*, preceeding paper in this issue.

(3) For a recent review of the transition metal catalyzed hydroboration reaction, see: Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* **1991**, *91*, 1179-1191.

(4) Männig, D.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 878-879.

(5) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(6) Kono, H.; Ito, K. *Chem. Lett.* **1975**, 1095-1096.

(7) For a preliminary account of this work, see: Evans, D. A.; Fu, G. C. *J. Org. Chem.* **1990**, *55*, 2280-2282.

(8) Burgess, K.; Donk, W. A.; Kook, A. M. *J. Org. Chem.* **1991**, *56*, 2949-2951.

(9) For studies of related systems, see: (a) Oxidative addition of alkylboranes to Ir(I): Baker, R. T.; Ovenall, D. W.; Calabrese, J. C.; Westcott, S. A.; Taylor, N. J.; Williams, I. D.; Marder, T. B. *J. Am. Chem. Soc.* **1990**, *112*, 9399-9400. (b) Ir(I) model system for catalyzed hydroboration: Knorr, J. R.; Merola, J. S. *Organometallics* **1990**, *9*, 3008-3010. (c) Reactions of catecholborane with rhodium complexes: Westcott, S. A.; Taylor, N. J.; Marder, T. B.; Baker, R. T.; Jones, N. J.; Calabrese, J. C. *J. Chem. Soc., Chem. Commun.* **1991**, 304-305.

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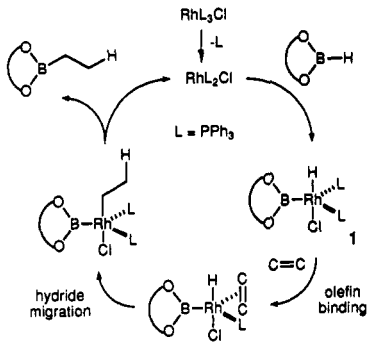
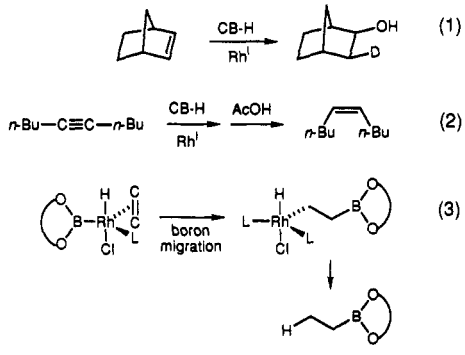


Figure 1. Männig–Nöth mechanism for the $Rh(PPh_3)_3Cl$-catalyzed hydroboration of olefins.

example, a model has recently been proposed to explain the diastereoselection observed in the hydroboration of chiral allylic alcohol and amine derivatives wherein irreversible binding of the diastereotopic faces of the alkene to rhodium is assumed to be the stereochemistry-determining step of this multistep transformation.[10] Without qualitative knowledge of the kinetic complexities of the catalyzed hydroboration reaction, this model represents little more than a mnemonic.

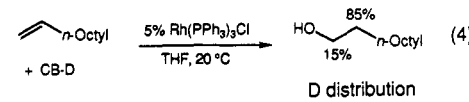
Results and Discussion

Before embarking on an in-depth study of the reaction mechanism, we carried out selected experiments designed to establish that the gross behavior of the catalyzed hydroboration process is consistent with the proposed pathway. In the first experiment, we found that the addition of mercury to the reaction medium does not poison the system, an observation consistent with the behavior expected for a homogeneous catalyst.[11] The possibility of a radical reaction was excluded since hydroboration proceeds smoothly in the presence of duroquinone, a species known to inhibit such processes.[12] Finally, the demonstration that catalyzed addition of the boron–hydrogen bond to both alkenes (eq 1) and alkynes (eq 2) occurs in a syn fashion is consistent with the premise that the reaction occurs at a single metal center and by conventional elementary steps.



On the basis of these data and precedent regarding related rhodium-catalyzed olefin addition reactions, the Männig–Nöth mechanism for the catalyzed hydroboration process (Figure 1) seems to be a reasonable one. In the following sections, we describe experiments that provide additional support for this pathway, including information regarding two important issues left unaddressed by Männig and Nöth: (1) the possibility that boron, rather than hydride, migrates to the bound olefin (eq 3; cf. Figure 1) and (2) the reversibility of the elementary steps of the catalytic cycle.

Deuterium Labeling Studies. Interest in pursuing labeling studies was stimulated by our observation that catalyzed hydroboration of 1-decene with deuteriocatecholborane (CB-D) furnishes 1-decanol wherein significant quantities of deuterium are found on the hydroxyl-bearing carbon (eq 4). This result is clearly inconsistent with the mechanism as originally presented, since simple hydrometalation requires that incorporation of a hydroxyl group at C_1 be coupled with that of deuterium at C_2 (Figure 1). However, this observation can be accommodated by the proposed pathway if the hydride migration step is in fact reversible (vide infra).[13]



This result prompted a detailed deuterium labeling study of the rhodium-catalyzed hydroboration of alkenes with CB-D. In the hope of gaining insight into the degree of reversibility both of the hydride migration and of the olefin binding steps, reactions were carried with a large excess of substrate. Hydroborations catalyzed by $Rh(PPh_3)_3Cl$ and $[Rh(nbd)(diphos\text{-}4)]BF_4$ generally afford qualitatively similar results; for the sake of brevity, only data for the former are discussed.[14]

Case 1: 1-Decene. Reaction of excess 1-decene with CB-D/$Rh(PPh_3)_3Cl$ leads to incorporation of deuterium not only in the α and β positions of the product alcohol[15] but in the recovered olefin as well (eq 5).[16] As suggested above, these results are most economically accommodated by the proposed catalytic cycle in which some of the elementary steps are reversible.

Six of the deuterium-containing compounds that one might expect to be produced if olefin complexation and hydride migration are reversible are depicted in the top and the bottom rows of Figure 2 (A, B, J–M). The four that are observed (cf. eq 5) are enclosed

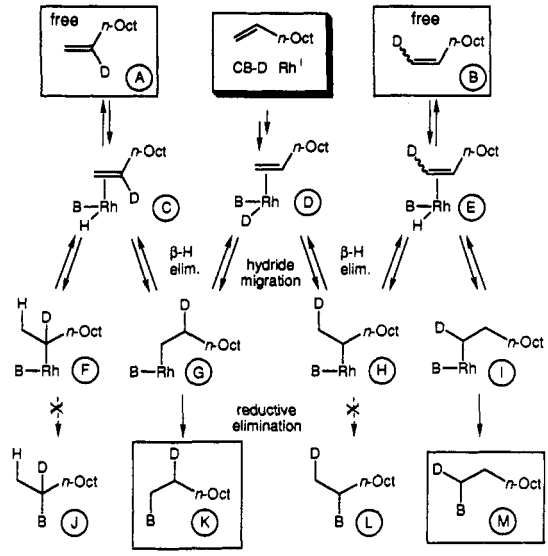
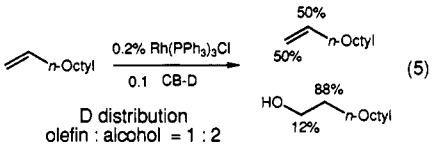


Figure 2. Deuterium labeling study of 1-decene (eq 5).

(10) Burgess, K.; Donk, W. A.; Jarstfer, M. B.; Ohlmeyer, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 6139–6144.
(11) Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855–859.
(12) Alberti, A.; Chatgilialoglu, C. *Tetrahedron* **1990**, *46*, 3963–3972.

(13) **Note**: Clearly, more complex mechanisms may be envisioned which also accommodate the results discussed in this section. We believe that our explanation (reversibility) has the merits of being both economical and reasonable. Obviously, if alternate pathways are in fact operative, then conclusions different from ours may be drawn.
(14) The discussion that follows is *qualitative* in emphasis. For example, by the "absence" of a particular product, we simply mean that it is not present in significant (>2%) quantities. Similarly, the term "irreversible" is not to be interpreted literally, but is instead intended to indicate that there is no manifestation of reversibility. A process that is labeled "rapid" relative to a subsequent step refers to a preequilibrium situation. Finally, we recognize that the use of CB-D introduces the possibility that isotope effects will impact upon the relative energies of the transition structures of the various elementary steps of the hydroboration process.
(15) No deuterium is detectible in the γ position, which suggests that scrambling is not occurring through a π-allyl complex, as has been proposed for rhodium- and iridium-catalyzed hydrogenation reactions. For leading references, see: Brown, J. M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 190–203.
(16) Only the deuterium-containing products are depicted. The percentages refer to the distribution of deuterium in the illustrated compound.



(5)

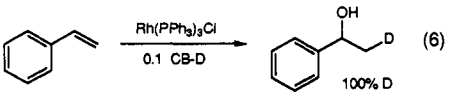
in boxes. Seven distinct processes of interest are illustrated in this diagram: (1) hydride migration to form a primary alkylrhodium (D → G); (2) hydride migration to form a secondary alkylrhodium (D → H); (3) β-hydride elimination of a primary alkylrhodium (G → D); (4) β-hydride elimination of a secondary alkylrhodium (H → D); (5) reductive elimination of a primary alkylboronate (G → K); (6) reductive elimination of a secondary alkylboronate (H → L); and (7) olefin decomplexation (C → A). As discussed below, both the presence and the absence of the possible labeled reaction products afford insight into the relative energetics of these processes.

The generation of 2-deuteriodec-1-ene (A) is readily accounted for by the sequence D → G → C → A, which involves hydride migration to form a primary alkylrhodium complex (D → G), β-hydride elimination of this primary alkylrhodium species to furnish a rhodium–terminal olefin complex (G → C), and release of olefin (C → A). Similarly, the formation of 1-deuteriodec-1-ene (B) may proceed by the pathway D → H → E → B, which entails hydride migration to afford a secondary alkylrhodium (D → H), β-hydride elimination of this secondary alkylrhodium (H → E), and decomplexation of the olefin (E → B). The presence of these deuterated decenes in the reaction mixture requires that olefin binding be reversible and that both of the possible hydride migration processes (D → G, D → H) occur, reversibly.

The observation that 1-deuteriodecan-1-ol is produced (via D → H → E → I → M) provides additional evidence for the viability of hydride migration to generate a secondary alkylrhodium species (D → H). The absence of product L, despite the accessibility of intermediate H, therefore indicates that reductive elimination of alkylboronates from secondary alkylrhodium complexes is slow compared to all other processes depicted in Figure 2. The relative sluggishness of this reductive elimination is thus responsible for the high level of regioselectivity observed in the $Rh(PPh_3)_3Cl$-catalyzed hydroboration of terminal olefins (1-ol:2-ol = 99:1).[2]

On the basis of the distribution of deuterium (eq 5), the following conclusions may also be drawn: (1) Decomplexation of olefin is not occurring rapidly relative to hydride migration. The generation of both B and M requires the intervention of olefin complex E. Were decomplexation rapid relative to migration ($k_{E\rightarrow B} \gg k_{E\rightarrow I}$), the ratio of B:M would approximately equal the overall ratio of olefin:alcohol (9:1). However, the observed ratio of B:M is ~2:1 (50:(2 × 12)). (2) Hydride migrations and β-hydride eliminations are not proceeding rapidly relative to reductive elimination of the primary alkylboronate. Were this not the case, deuterium would be distributed statistically between C_1 and C_2 in the product. Thus, of the seven processes of interest listed above, six are occurring with comparable facility during the catalyzed hydroboration of 1-decene, whereas one, reductive elimination of a secondary alkylboronate, is not observed.

Case 2: Styrene. The reaction of styrene provides an example of the profound influence that electronic effects may exert on the course of the catalyzed hydroboration process. In contrast to the case of 1-decene, the reaction of excess styrene with CB-D/Rh-$(PPh_3)_3Cl$ affords only one deuterium-containing product, 1-phenyl-2-deuterioethanol (eq 6).[17]



(6)

Figure 3 provides a graphical interpretation of this observation. The formation of 1-phenyl-2-deuterioethanol (L) is accounted for

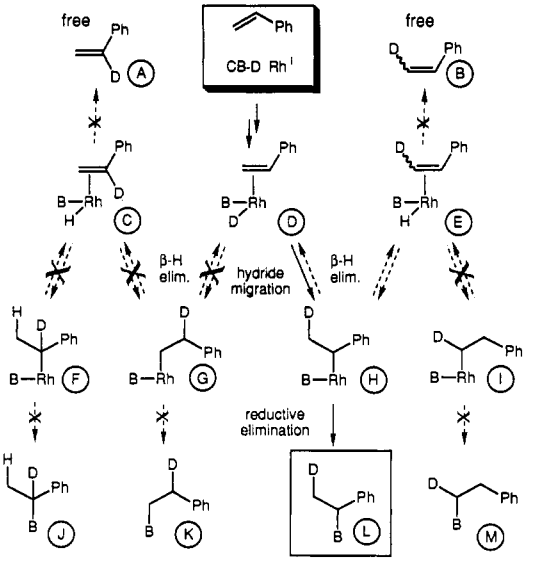


Figure 3. Deuterium labeling study of styrene.

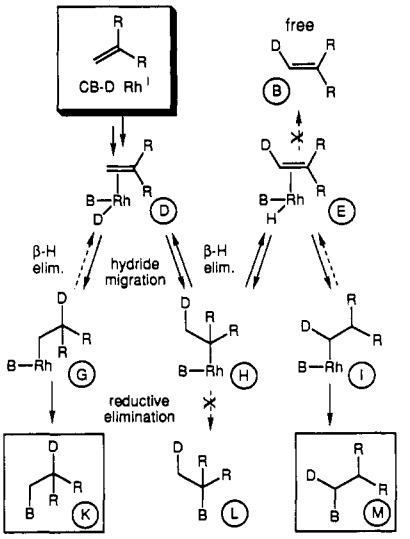
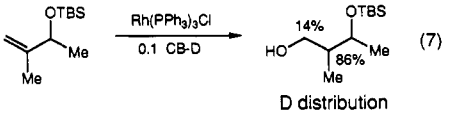


Figure 4. Deuterium labeling study of a 1,1-disubstituted olefin.

by hydride migration to generate a secondary, benzylic alkylrhodium complex (D → H), followed by reductive elimination of the secondary alkylboronate (H → L). The absence of β-deuteriostyrene (B) demands that β-hydride elimination from the alkylrhodium species (H → E) and styrene decomplexation (E → B) are not *both* occurring. The lack of deuterium incorporation α to the phenyl moiety demonstrates that hydride migration to form a primary alkylrhodium complex (D → G) is not a viable reaction pathway; thus, in sharp contrast to 1-decene, the regioselectivity observed in the catalyzed hydroboration of styrene is determined exclusively at the hydride migration step.

Case 3: 2-Methyl-3-[(*tert*-butyldimethylsilyl)oxy]but-1-ene. Hydroboration of this 1,1-disubstituted olefin with CB-D/Rh-$(PPh_3)_3Cl$ provides yet another qualitatively distinct result (eq 7). Figure 4 provides a graphical interpretation of this obser-



(7)

vation. The sequence D → G → K, which involves hydride migration to furnish a primary alkylrhodium complex (D → G) followed by reductive elimination of a primary alkylboronate (G → K), readily accounts for the formation of K. M is generated by the pathway D → H → E → I → M, which requires hydride migration to afford a tertiary alkylrhodium (D → H), β-hydride

(17) For references to an analogous turnover in regioselectivity in the rhodium-catalyzed hydroformylation of styrenes, see: Doyle, M. M.; Jackson, W. R.; Perlmutter, P. *Tetrahedron Lett.* **1989**, *30*, 5357–5360.

Table I. "Nonproductive" Elementary Steps Revealed by Deuterium Labeling Studies

	1-decene	styrene	1,1-olefin
olefin decomplexation?	Y	?	N
β-hydride elimination from the major[a] alkylrhodium?	Y	?	?
hydride migration to form the minor[b] alkylrhodium?	Y	N	Y
β-hydride elimination from the minor alkylrhodium?	Y	N	Y

[a] For styrene, "major" refers to the secondary alkylrhodium intermediate; for 1-decene and the 1,1-disubstituted olefin, it refers to the primary alkylrhodium. [b] For styrene, "minor" refers to the primary alkylrhodium intermediate; for 1-decene and the 1,1-disubstituted olefin, it refers to the secondary and the tertiary alkylrhodium, respectively.

elimination of the tertiary alkylrhodium to regenerate an olefin complex (H → E), hydride migration to form a primary alkylrhodium (E → I), and reductive elimination of a primary alkylboronate (I → M). The necessary intermediacy of H and E in this series of reactions, coupled with the absence of L and B in the product mixture, leads to the conclusion that reductive elimination of tertiary alkylboronate (H → L) and olefin decomplexation (E → B) are not viable under these conditions. In summary, we know the following with regard to the processes illustrated in Figure 4: (1) Hydride migration generates both the primary (D → G) and the tertiary (D → H) alkylrhodium complexes. (2) The tertiary alkylrhodium undergoes β-hydride elimination (H → E). (3) The high level of regioselectivity observed in the reaction (primary:tertiary alkylboronate = >99:1) may be attributed to the reluctance of the tertiary alkylrhodium species to reductively eliminate (H → L). (4) Olefin complexation is irreversible.

The course followed by the catalyzed hydroboration reaction is clearly substrate-dependent (Table I). This variability may lead to different selectivity-determining steps for different olefins; for example, the regioselectivity-determining step for the reaction of 1-decene is reductive elimination, whereas for styrene it is hydride migration. These cases underscore the fact that caution is warranted when extrapolating those conclusions drawn from study of a particular substrate to a broader range of compounds.

Irreversible Reductive Elimination. The deuterium labeling experiment described for 1-decene demonstrates that the elementary steps leading up to reductive elimination are reversible for this substrate (see case 1), but it does not address the issue of the reversibility of the reductive elimination itself. Therefore, an experiment was run in which 1-dodecene was hydroborated under the standard rhodium-catalyzed hydroboration conditions. After sufficient time to allow for complete alkylboron formation, 1-decene was added to the reaction. This mixture was stirred for 45 min and then subjected to oxidation. Were reductive elimination (and therefore the entire hydroboration sequence) reversible, one would expect to detect some 1-decanol in the final reaction mixture. Only 1-dodecanol was observed, thereby establishing that reductive elimination is indeed irreversible in the catalyzed hydroboration of aliphatic 1-alkenes.

Isomerization of Internal Olefins. The extent of isomerization in the catalyzed hydroboration of internal olefins was investigated in the hope of gaining additional insight into the reversibility of the elementary steps of the catalytic cycle.[18] As illustrated in Table II, only 4-octanol is formed in the hydroboration of *trans*-4-octene when $Rh(PPh_3)_3Cl$ is employed as the catalyst. The absence of regioisomeric alcohols indicates that isomerization does not occur under these conditions and, therefore, that hydride migration is essentially irreversible. This conclusion stands in stark contrast to the results of the deuterium labeling study of 1-decene discussed earlier, wherein hydride migration is shown to be reversible. Small quantities of isomeric alcohols are detected in the

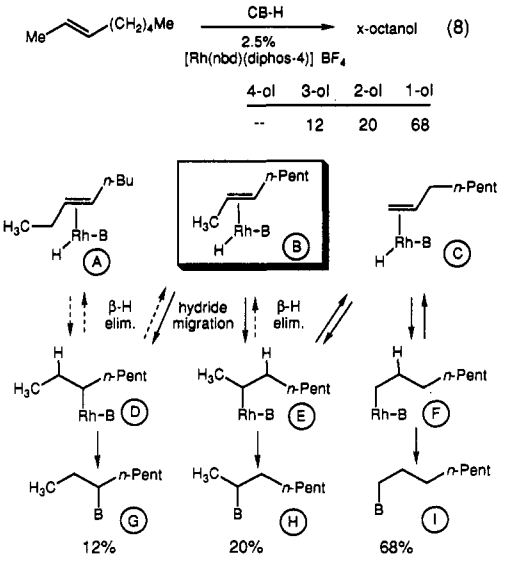
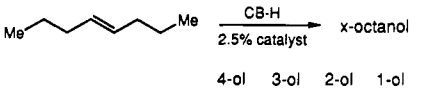


Figure 5. Hydroboration of *trans*-2-octene (eq 8).

Table II. Product Ratios for the Hydroboration of *trans*-4-Octene



	4-ol	3-ol	2-ol	1-ol
$Rh(PPh_3)_3Cl$	100	--	--	--
[Rh(nbd)(diphos-4)] BF_4	87	7	2	4

reaction catalyzed by [Rh(nbd)(diphos-4)]BF_4.[19]

In light of the labeling experiments, these data suggest that β-hydride elimination is sensitive to the steric requirements of the olefin being produced; i.e., whereas formation of a rhodium–terminal olefin complex occurs readily (1-decene), generation of a rhodium–internal olefin complex is less facile (*trans*-4-octene), relative to reductive elimination.[20]

To furnish support for this hypothesis, we examined the [Rh(nbd)(diphos-4)]BF_4-catalyzed hydroboration of *trans*-2-octene (eq 8, Figure 5).[21] The data reveal a significant level of discrimination in the hydride migration step ($k_{B\to E} > k_{B\to D}$), presumably reflecting a steric bias. The failure to detect appreciable quantities (>2%) of 4-octanol in this reaction, as well as the predominant generation of 1-octanol, is consistent with our earlier results. The minor hydride migration product preferentially reductively eliminates (D → G), since β-hydride elimination necessarily produces a rhodium–internal olefin complex. In contrast, the major migration product (E) has two readily available options: either reductive elimination (E → H) or β-hydride elimination to afford a rhodium–terminal olefin complex (E → C). The latter pathway presumably places this reaction in the same manifold as a catalyzed hydroboration of a terminal olefin (e.g., 1-decene), from which the terminal alcohol is expected to emerge as the major product.[22]

Hydride versus Boron Migration. Cases in which extensive deuterium scrambling is observed are more economically accommodated by a mechanism involving the migration of hydride, as opposed to boron, during the course of the transition metal catalyzed hydroboration process (Figure 1 versus eq 3). In a related

(18) In the absence of catecholborane, $Rh(PPh_3)_3Cl$ and [Rh(nbd)(diphos-4)]BF_4 do not isomerize olefins.

(19) [Rh(nbd)(diphos-4)]BF_4-catalyzed hydroboration of 7-tetradecene by 4,4,6-trimethyl-1,3,2-dioxaborinane (TMDB) predominantly affords the *primary* alcohol (ref 2). Clearly, the relative activation energies of the elementary steps of the hydroboration catalytic cycle can vary with substrate, with boron hydride, and with catalyst!

(20) For a review of the properties and reactions of Wilkinson's catalyst, see: Jardine, F. H. *Prog. Inorg. Chem.* **1981**, *28*, 63–202.

(21) Unexpectedly, the $Rh(PPh_3)_3Cl$-catalyzed reaction furnishes substantial quantities of 2-octanol.

(22) We do not expect to observe the 96:4 ratio of 1-ol to 2-ol reported in the preceding paper since direct formation of a primary alkylrhodium is not possible in the case of 2-octene.

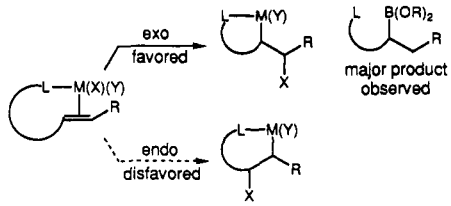


Figure 6. H versus B migration: implications of directed reactions.

system, Knorr and Merola recently furnished evidence for hydride migration during the Ir(I)-catalyzed addition of catecholborane to acetylenes.[9b]

The regioselectivity of the directed hydroboration reaction is also consistent with migration of hydride.[2] Delivered olefin addition reactions display a preference for formation of the exo product, presumably for stereoelectronic reasons (Figure 6). Comparison of the regioisomer resulting from this mode of addition with the major product of the phosphinite- or the amide-directed hydroboration reactions suggests that reductive elimination of an alkylboronate, and therefore migration of hydride, is occurring.[2]

Effect of Catalyst Oxidation. Confidence in the experiments described above is critically dependent on the integrity of the reagents. Ample literature precedent reveals the problems arising from the intervention of impurities in $Rh(PPh_3)_3Cl$-catalyzed systems.[20] In particular, several mechanistic studies involving olefin hydrogenation mediated by Wilkinson's catalyst have led to reports of rate constants and product distributions which were later determined to be artifacts of catalyst or substrate contamination. We have found that impurities likewise have a marked effect on the regioselection and deuterium labeling experiments of $Rh(PPh_3)_3Cl$-catalyzed hydroboration.

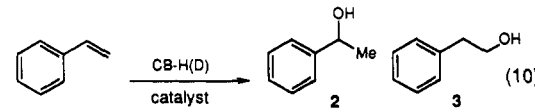
Wilkinson's catalyst is susceptible to contamination as a result of oxidation. The reaction of $Rh(PPh_3)_3Cl$ with oxygen in solution has long been known,[20,23] but oxidation upon prolonged standing in the solid phase has also been documented.[24] Rhodium–peroxo complexes have been reported to account for up to 40% of the metal species in some commercially available samples.[24] The dimeric rhodium compound shown in eq 9 is representative of several related oxidation products characterized from the reaction of Wilkinson's catalyst with oxygen.[23,24]

$$2\ RhCl(PPh_3)_3 \xrightarrow[CH_2Cl_2]{O_2} [Rh(PPh_3)_2Cl(O_2)]_2 \cdot sol + 2\ O{=}PPh_3 \qquad (9)$$

The regioselectivity of the $Rh(PPh_3)_3Cl$-catalyzed hydroboration of styrene with catecholborane has been the subject of several conflicting reports and serves to underscore the sensitivity of the system to catalyst purity. Published product distributions range from almost complete (>99:1) regioselectivity for the secondary alcohol **2**[7] to a 90:10 mixture favoring the primary alcohol **3**[25a] (eq 10, Table III). The involvement of an oxidized rhodium species has been suspected in a variety of $Rh(PPh_3)_3Cl$-catalyzed reactions in which oxygen, introduced either in a controlled fashion or by adventitious contamination, has a pronounced effect.[20,24,26] It was not unreasonable therefore to suspect that the cited inconsistencies might be the result of intervention by oxidized rhodium contaminants. This possibility was congruent with the observation of a decrease in the degree of regioselectivity for styrene hydroboration upon the use of "aged" Wilkinson's catalyst.[27]

In order to determine if catalyst oxidation was responsible for the differences in regioselectivities summarized in Table III,

Table III. Reported Regioselectivities of $Rh(PPh_3)_3Cl$-Catalyzed Hydroborations of Styrene (eq 10)



ref[a]	mol ratio: styrene	mol ratio: $C_6H_4O_2$ BH(D)[b]	mol ratio: $Rh(PPh_3)_3Cl$	product ratio 2:3
7 (this study)	10	1	0.02	>99:1
25b	1	2	0.02	86:4[c]
8	10	1	0.02	20:80
25a	1	1.1	0.01	10:90

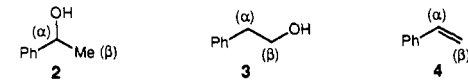
[a] All reactions were run in THF at room temperature unless otherwise noted. [b] CB-D used in refs 7 and 8. [c] Reaction run at 30 °C.

Table IV. Rh-Catalyzed Hydroboration of Styrene[a]

entry	catalyst	yield, %[b,c]	product ratio 2:3[b]
1	$Rh(PPh_3)_3Cl$	80	>99:1
2	$Rh(PPh_3)_3Cl$ O_2-treated	85	60:40
3	$[Rh(cod)Cl]_2$	45	20:80
4	$[Rh(cod)Cl]_2$, $2PPh_3$	67	60:40
5	$[Rh(cod)Cl]_2$, $4PPh_3$	90	98:2
6	$Rh(PPh_3)_3Cl$ (a) O_2-treated, (b) $2PPh_3$	85	>99:1

[a] Conditions: THF, 23 °C, 30 min; mol ratio of substrate: CB-H: catalyst = 1:2:0.01. Followed by basic peroxide oxidation. [b] Determined from the unpurified reaction mixture by capillary GC using a calibrated internal standard. [c] Combined yield of **2** and **3**.

Table V. Product and Deuterium Distribution for the Rhodium-Catalyzed Deuterioboration of Styrene (eq 10)



entry	conditions (ref)	2:3[a]	% D distribution[b]: 2 (α:β)	3 (α:β)	4 (α:β)
1	$Rh(PPh_3)_3Cl$ (this study)	>99:1	>95 (>95:5)	not observed	
2	$Rh(PPh_3)_3Cl$ (Burgess)[c]	20:80	14 (>99:1)	46 (60:40)	40 (10:90)
3	$Rh(PPh_3)_3Cl$ O_2-treated	22:78	16 (>95:5)	45 (60:40)	39 (10:90)

[a] Determined by capillary GC from the unpurified reaction mixture. [b] Determined by ^2H NMR from the unpurified reaction mixture. [c] Reference 8; reaction time = 30 min.

"oxidized" Wilkinson's catalyst was prepared by treatment with oxygen (eq 9)[23a,24] and employed as the catalyst for the hydroboration reaction.[28] The oxidized rhodium species proved to be an efficient hydroboration catalyst; however, the regioselectivity was dramatically altered, affording a 60:40 mixture of alcohols **2**/**3** (Table IV, entry 2). No differences in yield or product ratios were observed upon further exposure of the catalyst to oxygen for 45 min, verifying that catalyst oxidation is rapid. In contrast, when the solvent and the olefin were distilled immediately prior to use and freshly prepared catalyst was employed,[29] the catalyzed hydroboration of styrene exclusively afforded the secondary alcohol **2** (Table IV, entry 1).

(23) (a) Bennett, M. J.; Donaldson, P. B. *Inorg. Chem.* **1977**, *16*, 1585–1589. (b) Geoffroy, G. L.; Keeney, M. E. *Inorg. Chem.* **1977**, *16*, 205–207.

(24) Carvalho, M.; Wieserman, L. F.; Hercules, D. M. *Appl. Spectrosc.* **1982**, *36*, 290–296.

(25) (a) Hayashi, T.; Matsumoto, Y.; Ito, Y. *Tetrahedron: Asymmetry* **1991**, *2*, 601–612. (b) Zhang, J.; Lou, B.; Guo, G.; Dai, L. *J. Org. Chem.* **1991**, *56*, 1670–1672.

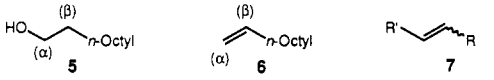
(26) (a) Augustine, R. L.; Van Peppen, J. F. *J. Chem. Soc., Chem. Commun.* **1970**, 495–496. (b) Augustine, R. L.; Van Peppen, J. F. *J. Chem. Soc., Chem. Commun.* **1970**, 571–572.

(27) Reactions run analogously to those that provided >99:1 selectivity for **2** using freshly prepared catalyst afforded a 1:1 mixture (**2**:**3**) when 1-year-old catalyst was employed; ≥3-year-old catalyst afforded a 1:4 (**2**:**3**) mixture. A. H. Hoveyda, Boston College, personal communication, 1991.

(28) The oxidation method was adapted from published procedures in which the Rh(III) oxidation products have been characterized by UV (ref 23b), X-ray photoelectron spectroscopy (ref 24), and X-ray crystallography (ref 23a).

(29) Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1967**, *10*, 67–71.

Table VI. Product and Deuterium Distribution for the Rhodium-Catalyzed Deuterioboration of 1-Decene



entry	catalyst (ref)	% D distribution[a] 5 (α:β)	6 (α:β)	6:7[b]
1	$Rh(PPh_3)_3Cl$ (this study)	67 (11:89)	33 (46:54)	≥95:5
2	$Rh(PPh_3)_3Cl$ (Burgess)[c]	*d*	*d*	5:≥95
3	$Rh(PPh_3)_3Cl$ O_2-treated	74 (16:84)	26 (48:52)	15:85
4	$Rh(PPh_3)_3Cl$ undistilled olefin	(16:84)		5:≥95
5	$Rh(PPh_3)_3Cl$ 3% *t*-BuO_2H[e]	79 (11:89)	21 (50:50)	70:30
6	$Rh(PPh_3)_3Cl$ (a) O_2-treated (b) $2PPh_3$	62 (11:89)	38 (44:56)	≥95:5

[a] Determined by ^2H NMR (46 MHz) from the unpurified reaction mixture. [b] Determined by ^1H NMR. [c] Reference 8; reaction time = 12 h. [d] Deuterium reported in all possible *CD* positions in **5** and **6**. [e] 3 mol % *t*-BuO_2H added prior to addition of CB-H.

The loss of regiocontrol that is observed for the styrene hydroboration reactions employing oxygen-treated $Rh(PPh_3)_3Cl$ or "aged" commercial samples is most likely due to catalysis by a ligand-deficient species. Oxidation of Wilkinson's catalyst has been shown to provide a mechanism for loss of triphenylphosphine as triphenylphosphine oxide.[23] Catalysis by a high oxidation state of rhodium is unlikely since catecholborane probably reduces the oxidized rhodium complexes to the active Rh(I) hydroboration catalyst.[30] Oxidation, however, is expected to result in reduced amounts of the triphenylphosphine ligand available for the active catalyst. Catalytic species of similar constitution were modeled by employing $[Rh(cod)Cl]_2$ as the catalyst and varying the amount of added triphenylphosphine.[31] Consistent with the observations of others,[8,25b] increases in the production of secondary alcohol are concomitant with increases in the PPh_3:Rh ratio (Table IV, entries 3–5). This hypothesis is convincingly supported by the demonstration that *high levels of regioselectivity can be restored for the oxygen-treated Wilkinson's catalysts by addition of triphenylphosphine* (PPh_3:Rh = 2; entry 6).

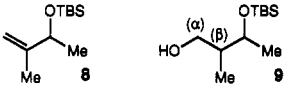
There have been other experimental inconsistencies reported for the $Rh(PPh_3)_3Cl$-catalyzed hydroboration reaction (Table V). Burgess and co-workers recently published deuterium labeling experiments[8] which contradicted the findings that were originally published from this laboratory.[7] We sought to resolve this issue cognizant of the influences that catalyst oxidation can have on the hydroboration reaction. Accordingly, when oxygen-treated Wilkinson's catalyst was employed for the reaction of CB-D with excess styrene, extensive deuterium scrambling was observed, and the sense of regioselectivity favored formation of the primary alcohol **3** (Table V, entry 3). These results parallel the product and deuterium distributions reported by Burgess (entry 2)[8] and suggest that catalyst contamination by oxidized rhodium species is responsible for the reported discrepancies between this and the Burgess study.

The hydroboration of 1-decene illustrates the sensitivity of the labeling study not only to catalyst contamination but also to substrate purity. Burgess reported extensive deuterium scrambling among all positions along the decyl chain of 1-decanol for the deuterioboration of 1-decene with CB-D (Table VI, entry 2).[8] In addition, randomly labeled internally isomerized decene isomers made up the majority of the recovered olefin (95%).

(30) ESCA measurements have shown that Rh(III) complexes prepared by oxygen treatment of Wilkinson's catalyst are reduced to Rh(I) complexes on treatment with $NaBH_4$ (see ref 24).

(31) Our results closely parallel those from experiments documented in ref 25b.

Table VII. Product and Deuterium Distribution for the Rh-Catalyzed Deuterioboration of **8**



entry	catalyst (ref)	% D distribution in **9**, β:α[a]
1	$Rh(PPh_3)_3Cl$ (this study)	83:17
2	$Rh(PPh_3)_3Cl$ (Burgess)[b]	>99:1
3	$Rh(PPh_3)_3Cl$ O_2-treated	>95:5
4	$Rh(PPh_3)_3Cl$ undistilled olefin	>95:5

[a] Determined by ^2H NMR (46 MHz). [b] Reference 8.

Although we have not found conditions under which random deuterium incorporation along the decyl chain of **5** occurs, we have been able to effect olefin isomerization by using either oxygen-treated Wilkinson's catalyst (Table VI, entry 3) or by employing freshly prepared catalyst and *undistilled* 1-decene (entry 4). The latter result suggests that the presence of allylic hydroperoxides leads to olefin isomerization, most likely as a result of catalyst oxidation.[20] This is supported by the observation that addition of *tert*-butyl hydroperoxide to the reaction mixture (3 mol %) also results in olefin isomerization (entry 5). Added triphenylphosphine inhibits isomerization when oxygen-treated catalyst is employed (entry 6 vs entry 3). These observations support the findings that treatment of Wilkinson's catalyst with oxygen accelerates olefin isomerization.[26a] Isomerization which occurs in olefin hydrogenation reactions mediated by oxygen-treated $Rh(PPh_3)_3Cl$ is also prevented by addition of triphenylphosphine.[26b]

Deuterioboration of 2-methyl-3-[(*tert*-butyldimethylsilyl)oxy]but-1-ene (**8**) is likewise affected by the presence of reagent and catalyst impurities (eq 7, Table VII). Only when freshly prepared catalyst and distilled substrate were employed was deuterium incorporated into the $C_1(\alpha)$-position of **9**. The use of oxygen-treated catalyst (entry 3) or undistilled olefin (entry 4) led to deuterium incorporation localized in the $C_2(\beta)$-position of **9**.

These experiments employing adulterated reagents provide added confidence that competing reactions mediated by contaminants did not obscure the fundamental processes monitored in the course of our deuterium labeling study.[7] The results provide a resolution to the disparities involving the published deuterium labeling studies[7,8] and are supported by a recent report from Burgess laboratory.[32] In this report, it is indicated that their original work was performed using commercial (i.e., "aged") Wilkinson's catalyst. When the hydroboration experiments of styrene and 1-decene were repeated using freshly prepared catalyst, product and deuterium distributions comparable to those described by this laboratory were obtained.

Conclusions

A sizable body of data has been accumulated which is consistent with a mechanism for the rhodium-catalyzed olefin hydroboration reaction that is analogous to that established for the corresponding hydrogenation process. The available evidence suggests that the reaction involves hydride, rather than boron, migration to the bound olefin. Isomerization and deuterium labeling studies have furnished insight into the relative facility, as well as the degree of reversibility, of the elementary steps of the hydroboration catalytic cycle; both aspects vary significantly according to substrate.

Experimental Section

General. Polymer-bound $Rh(PPh_3)_3Cl$ on styrene–divinylbenzene copolymer (2% cross-linked) was obtained from Strem. $Rh(PPh_3)_3Cl_3$,[33]

(32) Burgess, K.; Donk, W. A.; Kook, A. M. *J. Org. Chem.* **1991**, *56*, 7360.

$[Rh(cod)Cl]_2$,[34] and deuteriocatecholborane (CB-D)[35] were synthesized according to literature procedures. 1-Decene, styrene, and 2-methyl-3-[(*tert*-butyldimethylsilyl)oxy]but-1-ene were distilled from CaH_2 under reduced pressure and handled under N_2 immediately prior to use. Other general experimental procedures as well as the sources and purification methods for other reagents employed in this study have appeared elsewhere.[2]

Deuterioboration of Norbornene. CB-D (97 mg, 0.80 mmol) was added to a solution of $Rh(PPh_3)_3Cl$ (22.2 mg, 0.024 mmol) and norbornene (113 mg, 1.20 mmol) in 2.0 mL of THF. The reaction was stirred for 12 h at 20 °C and then subjected to a basic oxidative workup. Flash chromatography (25% EtOAc/hexane) afforded 77 mg (85%) of *exo*-2-norbornanol-*exo*-3-*d* as a white solid (identical by ^1H (the C_3 exo hydrogen resonance at δ 1.29 is absent) and ^{13}C NMR spectroscopy with material prepared by hydroborating norbornene with BD_3[36]). The corresponding reaction with $[Rh(nbd)(diphos\text{-}4)]BF_4$ (17.0 mg, 0.024 mmol) as catalyst afforded 72 mg (80%) of *exo*-2-norbornanol-*exo*-3-*d*.

Hydroboration–Protonolysis of 5-Decyne. CB-H (120 mg, 1.00 mmol) was added to a suspension of polymer-bound $Rh(PPh_3)_3Cl$[37] (50 mg) and 5-decyne (69 mg, 0.50 mmol) in 2.0 mL of THF. The resulting mixture was stirred at 20 °C for 5 h. The reaction was then filtered, and the solvent was removed under vacuum. Glacial AcOH (4 mL) was added, and the solution was stirred for 2.5 h at 80–115 °C. The reaction mixture was extracted (hexane/saturated NaCl), dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (hexane) yielded *cis*-5-decene as a colorless liquid (identical with material prepared by hydrogenating (Pd–$BaSO_4$) 5-decyne (TLC, ^1H NMR, and ^{13}C NMR). The reaction with $[Rh(nbd)(diphos\text{-}4)]BF_4$ as catalyst also afforded *cis*-5-decene.

Oxygen Treatment of $Rh(PPh_3)_3Cl$.[28] Oxygen was passed through a solution of $Rh(PPh_3)_3Cl$ in 2 mL of dichloromethane for 2 min. The solvent was removed in vacuo. Vacuum was maintained (≤0.1 Torr) for at least 30 min prior to use. Quantities of oxygen-treated catalyst refer to amounts of Wilkinson's catalyst prior to oxygen treatment.

Deuterioboration of 1-Decene; General Procedure. CB-D (48 mg, 0.40 mmol) was added to a mixture of the rhodium catalyst (0.008 mmol) and 1-decene (561 mg, 4.00 mmol) in 2.0 mL of THF (water bath). The resulting homogeneous solution was stirred for 1.5 h at 20 °C and then subjected to a neutral oxidative workup. The degree of olefin isomerization was monitored by ^1H NMR spectroscopy from the unpurified reaction mixture. ^2H NMR (46 MHz, $CHCl_3$) analysis of the unpurified reaction mixture provided the deuterium distribution among the reaction components (1-decanol:1-decene). The alcohol and the olefin were separated by chromatography. ^2H NMR analysis of the isolated 1-decanol indicated the ratio (decan-1-ol-*2-d*:decan-1-ol-*1-d*) of deuterium incorporation. Deuterium distributions thus determined are tabulated in Table VI of the text. Because the trace of decane that was produced in the reactions could not be separated from the decene by chromatography, the mixture of the two compounds was hydroborated with excess 9-BBN. The resulting 1-decanol was easily purified by chromatography. ^2H NMR analysis showed a 1:1 ratio (1-d:2-d) of deuterium incorporation. The corresponding reaction with $[Rh(nbd)(diphos\text{-}4)]BF_4$ (5.7 mg, 0.008 mmol) as catalyst afforded similar results.

Deuterioboration of Styrene. CB-D (48 mg, 0.40 mmol) was added to a mixture of $Rh(PPh_3)_3Cl$ (7.5 mg, 0.008 mmol) and styrene (416 mg, 4.00 mmol) in 2.0 mL of THF. The resulting homogeneous solution was stirred for 1.5 h at 20 °C and then subjected to a neutral oxidative workup. The ^2H NMR (46 MHz, $CHCl_3$) spectrum of the unpurified reaction mixture showed only 1-phenylethanol-*2-d*. Analysis of the unpurified reaction mixture by GC using a calibrated standard (1-octanol) indicated the ratio of secondary alcohol to primary alcohol was >99:1. The corresponding reaction with $[Rh(nbd)(diphos\text{-}4)]BF_4$ (5.7 mg, 0.008 mmol) as catalyst afforded identical results. Employing oxygen-treated $Rh(PPh_3)_3Cl$ (7.4 mg, 0.008 mmol) as catalyst afforded **2** in 16% yield, **3** in 56% yield, and ethylbenzene in 6% yield, as determined from the unpurified reaction mixture by GC using a calibrated standard (1-octanol). Relative distributions of deuterium-containing products were determined from the unpurified reaction mixture by ^2H NMR (46 MHz, $CHCl_3$) spectroscopy. Isolation by chromatography (10% EtOAc/hexane) and analysis by ^2H NMR gave the relative deuterium incorporation for each component. The values thus determined are given in Table V of the text.

Deuterioboration of 2-Methyl-3-[(*tert*-butyldimethylsilyl)oxy]but-1-ene; General Procedure. CB-D (48 mg, 0.40 mmol) was added to a mixture of $Rh(PPh_3)_3Cl$ (7.4 mg, 0.008 mmol) and olefin (802 mg, 4.00 mmol) in 2.0 mL of THF. The resulting homogeneous solution was stirred for 10 h at 20 °C and then subjected to a neutral oxidative workup. ^2H NMR (46 MHz, $CHCl_3$) analysis of the unpurified reaction mixture revealed the presence of deuterium α and β to the primary hydroxyl group, but showed no incorporation at the sp^2 carbon of the unreacted alkene. The alcohol and the olefin were separated by chromatography. ^2H NMR analysis of the isolated alcohol indicated an 86:14 ratio (β:α) of deuterium incorporation. The recovered olefin was contaminated with significant quantities of the derived alkane. Because the two could not be separated by chromatography, the mixture was hydroborated with excess BH_3. ^2H NMR analysis of the alcohol isolated from this reaction showed no deuterium incorporation. The corresponding reactions employing oxygen-treated $Rh(PPh_3)_3Cl$ (7.4 mg, 0.008 mmol) in one case and undistilled 2-methyl-3-[(*tert*-butyldimethylsilyl)oxy]-but-1-ene in another case were carried out and analyzed by identical methods to afford the alcohol product with exclusive (≥95%) deuterium incorporation in the β position. No deuterium incorporation was detected in the recovered olefin.

Irreversible Reductive Elimination. CB-H (120 mg, 1.00 mmol) was added to a solution of 1-dodecene (252 mg, 1.50 mmol) and $Rh(PPh_3)_3Cl$ (18.5 mg, 0.02 mmol) in 2.0 mL of THF. The resulting solution was stirred at 20 °C for 45 min, and then 1-decene (210 mg, 1.50 mmol) was added. This mixture was stirred at 20 °C for 45 min and then subjected to a basic oxidative workup. The products were analyzed by gas chromatography, which showed no 1-decanol (to the limits of detection). The corresponding reaction with $[Rh(nbd)(diphos\text{-}4)]BF_4$ as catalyst afforded similar results.

Octene (2-Octene and 4-Octene) Isomerization; General Procedure. CB-H (240 mg, 2.00 mmol) was added to a mixture of olefin (112 mg, 1.00 mmol) and catalyst (0.025 mmol) in 1.5 mL of $ClCH_2CH_2Cl$. The resulting homogeneous solution was stirred at 20 °C for 12 h and then subjected to a basic oxidative workup. Aliquots of the reaction mixture were analyzed by gas chromatography.

Styrene Hydroboration, Regioselectivity; General Procedure. CB-H (240 mg, 2.00 mmol) was added to a mixture of rhodium catalyst (0.010 mmol) and styrene (104 mg, 1.00 mmol) in 2.0 mL of THF. The resulting solution was stirred for 30 min at 20 °C and then subjected to a basic oxidative workup. The mixtures were analyzed without further purification by ^1H NMR spectroscopy and GC. Yields and product ratios were determined from the unpurified reaction mixture by GC using a calibrated standard (1-octanol). Rhodium catalysts, product ratios, and yields are given in Table IV of the text. The corresponding reaction with $[Rh(nbd)(diphos\text{-}4)]BF_4$ (7.1 mg, 0.01 mmol) as catalyst afforded a >99:1 (secondary:primary) ratio of alcohols.

Acknowledgment. Support has been provided by the NIH. The NIH BRS Shared Instrumentation Grant Program (1 S10 RR01748-01A1) is acknowledged for providing NMR facilities.

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(36) Lambert, J. B.; Greifenstein, L. G. *J. Am. Chem. Soc.* **1974**, *96*, 5120–5124.
(37) Polymer-bound $Rh(PPh_3)_3Cl$ was employed in order to minimize the possibility of rhodium-catalyzed side reactions intervening in the acetic acid protonolysis.