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)(PCy3)(py)]PF6 (8.0 mg, 0.01 mmol) in 1.0 mL of CIC-H2=CH2Cl. 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-[(N-phenylmethyl)carbamoyl]-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-cyclohexenylcarboxyl)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.

Hydroboronation 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 CIC=CH2Cl. The resulting mixture was stirred at 20 °C for 30 min and then cooled to 0 °C and stirred under vacuum for 25 min.46 The reaction was then warmed to 20 °C, and [Ir(cod)(PCy3)(py)]PF6 (16.0 mg, 0.02 mmol) was added. The mixture immediately turned homogenous, 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 MgSO4, filtered, and concentrated. An aliquot was analyzed by GLC, which showed 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)pentaenamide: R = 0.20 (EtOAc); IR (KBr) 3300, 2970, 2930, 1650, 1550, 1453, 1310, 1030 cm⁻¹;1H NMR (400 MHz, CDCl3) δ 7.25–7.40 (m, 5 H, aromatic H), 6.09 (br s, 1 H, NH), 4.42 (d, 2 H, J = 5.7 Hz, CH2Ph), 3.84 (m, 1 H, CHOH), 2.38 (dt, 2 H, J = 2.3, 7.0 Hz, CH2CO), 1.84 (m, 1 H, CH2CH2OH), 1.71 (m, 1 H, CH2CHOH), 1.20 (3, 3 Hz, J = 6.2 Hz, CH2);23C NMR (75 MHz, CDCl3) δ 173.34, 138.20, 128.72, 127.79, 127.52, 67.52, 147.36, 34.30, 33.18, 23.66; HRMS m/z calcd for C7H7N2O2 (M+) 208.1338, found 208.1346.

5-Hydroxy-N-(phenylmethyl)pentaenamide: R = 0.15 (EtOAc); IR (CHCl3) 3450, 3430, 3010, 2940, 1665, 1515, 1455, 1235 cm⁻¹; 1H NMR (300 MHz, CDCl3) δ 7.25–7.40 (m, 5 H, aromatic H), 5.77 (br s, 1 H, NH), 4.46 (d, 2 H, J = 5.7 Hz, CH2Ph), 3.66 (q, 2 H, J = 5.8 Hz, CH2OH), 2.28 (t, 1 H, J = 7.1 Hz, CH2CO), 1.55–1.85 (m, 5 H, CH2CH2-CH2OH);13C NMR (75 MHz, CDCl3) δ 173.12, 138.35, 128.61, 127.69, 127.39, 61.89, 43.54, 35.97, 31.95, 21.79. Anal. Calcd. for C12H18N2O2: 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.

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.

Support for this pathway was provided by their observation that adduct 1, first isolated by Kono and Ito, reacts stoichiometrically with olefins to afford hydroboration products.6

While significant effort has been focused on the catalyzed hydroboration reaction as a synthetic method,2,3,69 few investigations have probed the mechanistic details of this process.3,7,79 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

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(PPh3)3Cl-catalyzed hydroboration (Figure 1) which is analogous to that proposed for other, more thoroughly investigated rhodium-catalyzed olefin addition reactions such as hydrogenation, hydrosilylation, and hydroformylation.2

(49) It is necessary to remove H2 from the reaction system prior to addition of the catalyst in order to minimize substrate hydrogenation.
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 stereocchemistry-determining step of this multistep transformation. 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. The possibility of a radical reaction was excluded since hydroboration proceeds smoothly in the presence of duroquinone, a species known to inhibit such processes. 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.

\[
\text{eq 1: } \text{CB}-H \rightarrow \text{R}^1 \\
\text{eq 2: } \text{CB}-H \rightarrow \text{R}^1 \text{OH} \rightarrow \text{R}^1 \\
\text{eq 3: } \text{boron migration} \rightarrow \text{olefin binding} \\
\]

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 deutericcataloborane (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 C1 be coupled with that of deuterium at C2 (Figure 1). However, this observation can be accommodated by the proposed pathway if the hydride migration step is in fact reversible (vide infra). 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.

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(PPh3)3Cl and [Rh(nbd)(diphos-4)]BF4 generally afford qualitatively similar results; for the sake of brevity, only data for the former are discussed.

**Case I: 1-Decene.** Reaction of excess 1-decene with CB-D/Rh(PPh3)3Cl leads to incorporation of deuterium not only in the α and β positions of the product alcohol but in the recovered olefin as well (eq 5). As suggested above, these results are most economically accomplished 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 bottom rows of Figure 2 (A, B, -M). The four that are observed (cf. eq 5) are enclosed in red squares.

\[
\text{eq 5: } \text{hydroboration of 1-decene} \\
\]

---

*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.

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 decomposition (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-deuteriododec-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-deuteriododec-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 decaenes 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-deuteriododecan-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(PPh₃)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 decomposition rapid relative to migration (Kₑₖₑ > Kₑ₋ₑ⁻), 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 C₁ and C₂ 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-PPh₃Cl affords only one deuterium-containing product, 1-phenyl-2-deuterioethanol (eq 6).³⁷

Figure 3 provides a graphical interpretation of this observation. The formation of 1-phenyl-2-deuterioethanol (L) is accounted for 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-deuterostyrene (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-butyldimethylsilyloxy]but-1-ene. Hydroboration of this 1,1-disubstituted olefin with CB-D/Rh-PPh₃Cl provides yet another qualitatively distinct result (eq 7). Figure 4 provides a graphical interpretation of this obser-

---

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 alkylrhodium ≫ 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 (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.

Isoomerization 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. As illustrated in Table II, only 4-octanol is formed in the hydroboration of trans-4-octene when Rh(PPh₃)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 reaction catalyzed by [Rh(nbd)(diphos-4)]BF₄ (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–terminal olefin complex is less facile (trans-4-octene), relative to reductive elimination (20).

For support of this hypothesis, we examined the [Rh(nbd)(diphos-4)]BF₄-catalyzed hydroboration of trans-2-octene (eq 8, Figure 5). The data reveal a significant level of discrimination in the hydride migration step (k₈→E > k₈→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–terminal 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.

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(PPh₃)₃Cl and [Rh(nbd)(diphos-4)]BF₄ do not isomerize olefins.
The regioselectivity of the directed hydroboration reaction is also consistent with migration of hydride. 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 alkylborane, and therefore migration of hydride, is occurring.

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(PPh₃)₃Cl-catalyzed systems. 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(PPh₃)₃Cl-catalyzed hydroboration.

Wilkinson's catalyst is susceptible to contamination as a result of oxidation. The reaction of Rh(PPh₃)₃Cl with oxygen in solution has long been known, but oxidation upon prolonged standing in the solid phase has also been documented. Rhodium-peroxo complexes have been reported to account for up to 40% of the metal species in some commercially available samples. 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.

![Figure 6](image_url)

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

### Table IV. Rh-Catalyzed Hydroboration of Styrene

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Yield, %</th>
<th>Product Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rh(PPh₃)Cl</td>
<td>80</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>2</td>
<td>O₂-treated Rh(PPh₃)Cl</td>
<td>85</td>
<td>60:40</td>
</tr>
<tr>
<td>3</td>
<td>[Rh(cod)Cl]₂</td>
<td>45</td>
<td>20:80</td>
</tr>
<tr>
<td>4</td>
<td>[Rh(cod)Cl]₂, 2PPh₃</td>
<td>67</td>
<td>60:40</td>
</tr>
<tr>
<td>5</td>
<td>[Rh(cod)Cl]₂, 4PPh₃</td>
<td>90</td>
<td>98:2</td>
</tr>
<tr>
<td>6</td>
<td>Rh(PPh₃)Cl</td>
<td>85</td>
<td>&gt;99:1</td>
</tr>
</tbody>
</table>

*a Conditions: THF, 23 °C, 30 min; mol ratio of substrate: CB-H = 1:2:0.01. Followed by basic peroxide oxidation.

*b Determined from the unpurified reaction mixture by capillary GC using a calibrated internal standard.

### Table V. Product and Deuterium Distribution for the Rhodium-Catalyzed Deuteriohydroboration of Styrene

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions (ref)</th>
<th>% D Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rh(PPh₃)Cl</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>2</td>
<td>O₂-treated Rh(PPh₃)Cl</td>
<td>60:40</td>
</tr>
<tr>
<td>3</td>
<td>Rh(PPh₃)Cl</td>
<td>22:78</td>
</tr>
</tbody>
</table>

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

"oxidized" Wilkinson's catalyst was prepared by treatment with oxygen (eq 9) and employed as the catalyst for the hydroboration reaction. 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, the catalyzed hydroboration of styrene exclusively afforded the secondary alcohol 2 (Table IV, entry 1).

References:

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

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst (ref)</th>
<th>% D distribution&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(α:β)</td>
<td>(α:β)</td>
</tr>
<tr>
<td>5</td>
<td>Rh(PPh₃)Cl (this study)</td>
<td>67</td>
</tr>
<tr>
<td>6</td>
<td>Rh(PPh₃)Cl (Burgess)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>d</td>
</tr>
<tr>
<td>3</td>
<td>Rh(PPh₃)Cl; O₂-treated</td>
<td>16:84</td>
</tr>
<tr>
<td>4</td>
<td>Rh(PPh₃)Cl; undistilled olefin</td>
<td>16:84</td>
</tr>
<tr>
<td>5</td>
<td>Rh(PPh₃)Cl; 3% t-BuOH·H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>79</td>
</tr>
<tr>
<td>6</td>
<td>Rh(PPh₃)Cl; α-O₂-treated</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>(b) 2PPh₃</td>
<td>(11:89)</td>
</tr>
</tbody>
</table>

<sup>a</sup>Determined by <sup>2</sup>H NMR (46 MHz) from the unpurified reaction mixture.  <sup>b</sup>Determined by <sup>2</sup>H NMR.  <sup>c</sup>Reference 8; reaction time = 12 h.  <sup>d</sup>Deuterium reported in all possible C-D positions in 5 and 6.  <sup>e</sup>3 mol % t-BuOH·H₂ added prior to addition of CB-H.

The loss of regiocontrol that is observed for the styrene hydrosilation reactions employing oxygen-treated Rh(PPh₃)Cl 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 triphenylphosphate oxide.  <sup>23</sup> 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.  <sup>20</sup> 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(ocd)Cl]₂ as the catalyst and varying the amount of added triphenylphosphate.  <sup>31</sup> Consistent with the observations of others,  <sup>8</sup> the production of secondary alcohol is concomitant with increases in the PPh₃: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 "aged" Wilkinson's catalyst by addition of triphenylphosphine (PPh₃:Rh = 2; entry 6).

There have been other experimental inconsistencies reported for the Rh(PPh₃)Cl-catalyzed hydrosilation reaction (Table V). Burgess and co-workers recently published deuterium labeling experiments  <sup>8</sup> which contradicted the findings that were originally published from this laboratory.  <sup>7</sup> We sought to resolve this issue cognizant of the influences that catalyst oxidation can have on the hydrosilation 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)  <sup>8</sup> and suggest that catalyst contamination by oxidized rhodium species is responsible for the reported discrepancies between this and the Burgess study.

The hydrosilation 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 VII, entry 2). In addition, randomly labeled internally isomerized decen-3-one 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 NaBH₄ (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

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst (ref)</th>
<th>% D distribution in 9, βα&lt;sup&gt;b&lt;/sup&gt;</th>
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<tbody>
<tr>
<td>1</td>
<td>Rh(PPh₃)Cl</td>
<td>83:17</td>
</tr>
<tr>
<td>2</td>
<td>Rh(PPh₃)Cl</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>3</td>
<td>Rh(PPh₃)Cl</td>
<td>&gt;95:5</td>
</tr>
<tr>
<td>4</td>
<td>Rh(PPh₃)Cl</td>
<td>&gt;95:5</td>
</tr>
</tbody>
</table>

<sup>a</sup>Determined by <sup>2</sup>H NMR (46 MHz).  <sup>b</sup>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 aliphatic hydroperoxides leads to olefin isomerization, most likely as a result of catalyst oxidation.  <sup>20</sup> 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.  <sup>26b</sup> Isomerization which occurs in olefin hydrogenation reactions mediated by oxygen-treated Rh(PPh₃)Cl is also prevented by addition of triphenylphosphine.  <sup>26b</sup>

Deuterioboration of 2-methyl-3-[(tert-butyl(dimethyl)silyl)-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 C₁(α)-position of 9. The use of oxygen-treated catalyst (entry 3) or undistilled olefin (entry 4) led to deuterium incorporation localized in the C₁(β)-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.  <sup>7</sup> The results provide a resolution to the disparities involving the published deuterium labeling studies  <sup>1-6</sup> and are supported by a recent report from Burgess laboratory.  <sup>22</sup> In this report, it is indicated that their original work was performed using commercial (i.e., "aged") Wilkinson's catalyst. When the hydrosilation 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 hydrosilation 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 hydrosilation catalytic cycle; both aspects vary significantly according to substrate.

Experimental Section

General. Polymer-bound Rh(PPh₃)Cl on styrene-divinylbenzene copolymer (2% cross-linked) was obtained from Streml. Rh(PPh₃)Cl,  <sup>33</sup>
Mechanistic Study of Catalyzed Hydroborations

[Rh(cod)Cl]2 and deuterioacetochelaborane (CB-D)3 were synthesized according to literature procedures. 1-Decene, styrene, and 2-methyl-3-[(tert-butyldimethylsilyloxy)but-1-ene were distilled from CaH2 under reduced pressure and handled under N2 immediately prior to use. Other general experimental procedures as well as the sources and purification methods for other reagents employed in this study have been described elsewhere.2

Deuterioboration of Norbornene. CB-D (97 mg, 0.80 mmol) was added to a solution of Rh(PPh3)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 with material prepared by hydrogenating Rh(PPh3)Cl5.5 and deuteriocatecholborane (CB-D)3S were synthesized according to literature procedures. 1-Decene, styrene, and 2-methyl-3-[(tert-butyldimethylsilyloxy)but-1-ene were distilled from CaH2 under reduced pressure and handled under N2 immediately prior to use. Other general experimental procedures as well as the sources and purification methods for other reagents employed in this study have been described elsewhere.2

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