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Further Evidence for the Role of $d\pi$-$p\pi$ Bonding in Rhodium-Mediated Hydroborations

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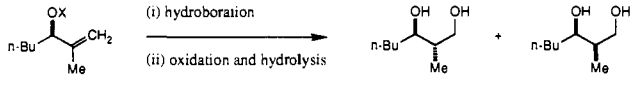
Abstract: Stereoelectronic effects governing coordination of the alkene functionality to rhodium have been postulated to account for diastereofacial selectivities in catalyzed hydroborations of allylic alcohol derivatives **1**; this paper describes two sets of experiments to test this controversial hypothesis. The first one involves competition experiments between related allylic alcohol derivatives, and shows that allylic trifluoroacetates react at least 160–210 times faster than allylic acetates under the catalyzed conditions. Similar competition experiments with uncatalyzed hydroborations reveal rate differences of less than 5-fold in the opposite sense (i.e. allylic acetates react faster). The second set of experiments show that catalyzed and uncatalyzed hydroborations of 5-substituted 2-methyleneadamantanes **5** proceed with opposite diastereofacial selectivities. Results from the competition experiments and the stereoselectivity studies are consistent with the original postulate for stereoelectronic effects in catalyzed hydroborations, and provide pointers to some of the mechanistic features that characterize the process. Experiments to probe the reversibility of mechanistic steps in rhodium-catalyzed hydroborations are presented. Finally, selectivities observed in the catalyzed hydroborations of 5-substituted 2-methyleneadamantanes **5** are discussed with reference to the "Cieplak postulate", a hypothesis that is shown to be inappropriate for predicting the stereochemical outcome of catalyzed hydroborations.

Introduction

One of the most significant observations to emerge from recent studies of rhodium-mediated hydroboration reactions is that catalyzed hydroborations of the allyl alcohol derivatives **1** give syn products **2** selectively, whereas uncatalyzed reactions preferentially give the anti isomers.[1-3] Similarly, catalyzed and uncatalyzed hydroborations of allylamine derivatives tend to be syn and anti selective, respectively.[4,5]



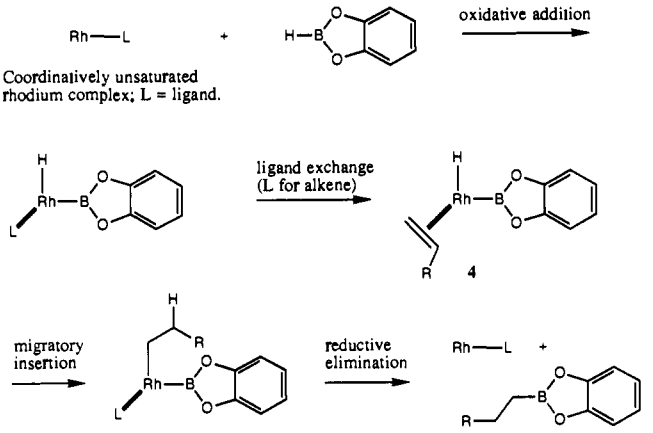
1 *anti*-**2** *syn*-**2**

X	$HBO_2C_6H_4$, Rh-cat *syn:anti*	9-BBN *syn:anti*
$COCH_3$	2.7:1.0	1.0:7.5
$COCF_3$	7.5:1.0	1.0:14
CO^tBu	6.5:1.0	1.0:15

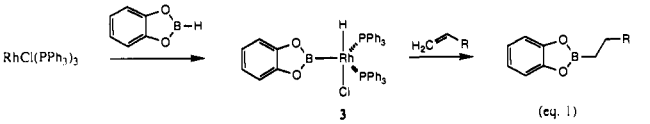
The origin of this "stereocomplementary" behavior is an enigma in contemporary organic chemistry, and one that is difficult to address because the details of the mechanism of catalyzed hydroborations are unknown. However, the generalized reaction pathway shown in Scheme I seems reasonable,[6] particularly when compared with the related, and much better understood, rhodium-promoted *hydrogenation* reactions.[7,8]

Further support for the mechanism postulated in Scheme I is derived from some stoichiometric reactions of transition-metal

Scheme I. Generalized Mechanism for Catalyzed Hydroborations



complexes, which resemble steps in the proposed catalytic cycle. For instance, catecholborane oxidatively adds to $RhCl(PPh_3)_3$ giving complex **3**, which combines with alkenes to give hydroboration products (eq 1).[6,9] Furthermore, migratory insertion



3 (eq. 1)

of alkynes into the iridium–hydride bond of a borylhydridoiridium complex has been observed,[10,11] and reductive elimination of vinyl

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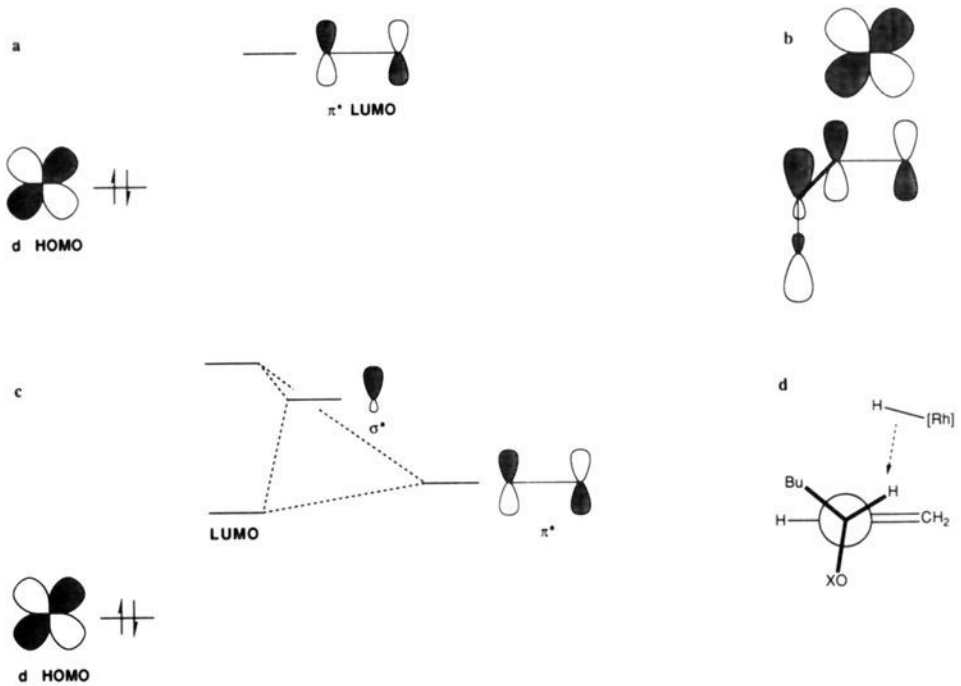
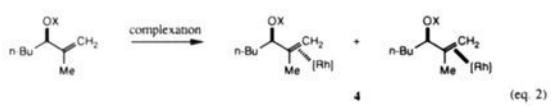


Figure 1. (a) Primary interaction in coordination of an alkene to a transition-metal complex. (b) Orbitals involved in the secondary interaction, and the orientation required to achieve overlap. (c) Secondary interaction lowers the LUMO level relative to the primary interaction alone. (d) Proposed reactive conformation in rhodium-mediated hydroborations of allylic alcohols **1**.

and boryl ligands from an iridium complex is known.[12]

Two diastereomers can arise from complexation of a chiral alkene to a transition metal. Recently, two of us suggested that substrate-controlled diastereoselectivity in catalyzed hydroborations of the allylic alcohol derivatives **1** and related substrates may be dictated by the face selectivity of complexation in the formation of such η^2-alkene complexes (eq 2).[3,13] Inherent in this hypothesis



4 (eq 2)

is the assumption that the minor diastereomer formed on complexation does not react quickly to give the major stereoisomer of the product, i.e. the peculiar type of situation observed in rhodium-mediated *hydrogenations* of dehydroamino acids[8] is *not* applicable. On the basis of this assumption it is possible to account for diastereoselectivities observed in catalyzed hydroborations of allylic alcohols **1** by considering steric and electronic effects. Frontier orbitals controlling metal complexations of the type depicted in eq 2 (Figure 1a) are perturbed if one substituent of the chiral center is aligned perpendicular to the alkene, such that a σ^*-orbital at that chiral center overlaps with the π^*-orbital of the alkene (Figure 1b); this reduces the HOMO–LUMO energy gap (Figure 1c). *Maximum stabilization of the metal-to-alkene π-bond therefore will be achieved when the most electron-withdrawing substituent (OX) is placed in the anti position*, because this provides the lowest energy σ^*-orbital for mixing with the alkene π^*-orbital. On the basis of steric effects, the smallest of the other two substituents at the chiral center (H in this example) will preferentially occupy the "inside crowded"[14] position in the metal–alkene complex, thus avoiding steric interactions between the rhodium center and the larger group "R". Consequently, one would predict that allylic alcohols **1** in catalyzed hydroborations react predominantly via the conformation shown in Figure 1d.[3,13]

The terms "kinetic control" and "thermodynamic control" are ambiguous when applied to multistep processes like that depicted in Scheme I. If the relative rates of the steps are such that complexation of the alkene is effectively irreversible, then the frontier-orbital argument presented above may be applied to predict which diastereomeric alkene complex **4** is formed fastest. Conversely, if the diastereomeric complexes are rapidly interconverting, the orbital rationale provides a means to assess which is more stable; the observed selectivities could then be a consequence of a weighted equilibrium between two diastereomeric complexes that rapidly interconvert via a metal species without π-alkene ligands. Intuitively, we would predict that the complexation event is reversible.

In any event, the orbital hypothesis can also be used to explain the 3-fold increase in syn selectivity observed on changing the protecting group from acetate (**1**, X = $COCH_3$) to trifluoroacetate (X = $COCF_3$): the σ^*-orbital associated with C–$OCOCH_3$ bonding is higher in energy than that corresponding to the C–$OCOCF_3$ linkage, mixing with the alkene π^*-orbital is better in the latter case, and the preference for the reactive conformation (or bonding orientation) shown in Figure 1b is accentuated. Conversely, increased syn selectivity for the pivalate (**1**, X = CO^tBu) relative to the acetate (X = $COCH_3$) is probably due to steric repulsion between the ester and the metal center, which reinforces the electronic preference for placing the ester group in the anti position.[3]

The predictive value of the hypothesis described above is proven,[3-5,13] but further evidence for the underlying concepts is desirable; consequently, we designed experiments to test two consequences of the theory outlined above, namely (i) increasing the electron-withdrawing capacity of the OX group of substrates **1** should *accelerate catalyzed hydroborations*, since this increases the affinity of the alkene for the metal (Figure 1c),[15] and (ii) catalyzed hydroborations of rigid substrates with electronically perturbed, but sterically equivalent, alkene faces should occur via preferential delivery of the boron hydride opposite the face flanked by the best σ-acceptor. Thus, two different sets of experiments were performed to probe these issues: (i) competition experiments using related, but electronically distinct, allylic alcohol derivatives,

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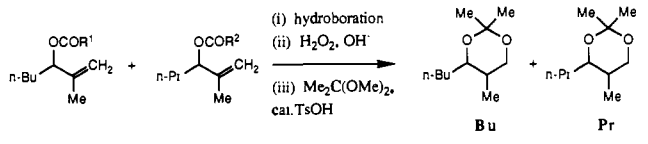
(15) If complexation of the alkene is reversible, then the overall reaction will be accelerated due to the increased concentration of the rhodium-alkene complex relative to the uncomplexed form (a consequence of the orbital effects). Alkenes with low energy π^*-orbitals are relatively good ligands: Tolman, C. A. *J. Am. Chem. Soc.* **1974**, *96*, 2780.

Table I. Relative Rates of Hydroborations of Allylic Alcohol Derivatives **1**



entry	R^1	R^2	conditions	Bu:Pr[a]
1	Me	Me	catalyzed[b]	1.0:1.2
2	Me	CF_3	catalyzed	1:160
3	CF_3	Me	catalyzed	210:1
4	CF_3	Me	uncatalyzed[c]	1.0:4.9
5	Me	*t*-Bu	catalyzed	2.7:1.0
6	*t*-Bu	Me	catalyzed	1.0:3.5

[a] Products formed as diastereomeric mixtures, but the ratios quoted are Bu(syn + anti):Pr(syn + anti); determined via capilliary GC and corrected for the detector's response to each compound. [b] Substrate: catecholborane 1.00:0.05, 0.5 mol % $RhCl(PPh_3)_3$, 25 °C, 12 h; oxidation with H_2O_2/OH^-, 25 °C, 12 h; the oxidation mixtures were extracted with diethyl ether, the combined extracts dried over sodium sulfate, and treated with excess 2,2-dimethoxypropane and catalytic 4-methylbenzenesulfonic acid at 25 °C for 2 h. [c] Hydroboration performed using 0.05 equiv of 9-BBN and processed as described in note *b*.

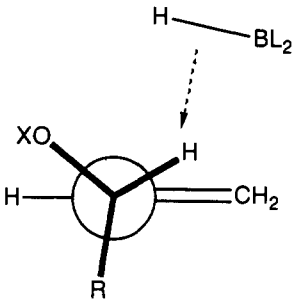


Figure 2. Preferred reactive conformation in uncatalyzed hydroborations of allylic alcohol derivatives **1**.

and (ii) a comparison of catalyzed and uncatalyzed hydroborations of 5-substituted 2-methyleneadamantanes.

Competition Experiments

A corollary to our model for stereocontrol in rhodium-catalyzed hydroborations of allylic alcohol derivatives is that the rate of catalyzed hydroborations of substrates **1** should increase with the electron-withdrawing capacity of the OCOR substituent (vide supra). Data from competition experiments designed to test this assertion are given in Table I. Near equimolar mixtures of the indicated substrates were hydroborated with 0.05 equiv of catecholborane, oxidized and treated with 2,2-dimethoxypropane, and the ratios of the acetonide products were measured by GC. This protocol establishes *minimum* rate ratios since those observed are less than the actual values due to approximations inherent in competition experiments of this type (i.e. concentrations of reactants were assumed to be constant at low conversions).

Entry 1 of Table I proves replacement of *n*-butyl with *n*-propyl has no significant effect on the rate of hydroboration. Substitution of an acetate protecting group with a trifluoroacetate, however, causes a rate enhancement of more than 150-fold (entries 2 and 3). A similar competition experiment to probe uncatalyzed hydroborations of the same substrates is depicted in entry 4; here the acetate reacts approximately 4 times *faster* than the trifluoroacetate. This is not surprising since electrophilic attack of a borane on an alkene is not expected to be facilitated by mixing of C–OCOR orbitals with the π-system (Figure 2);[16,17] indeed, uncatalyzed hydroborations of alkenes **1** should be slightly retarded when the σ-electron-withdrawing properties of the allylic ester

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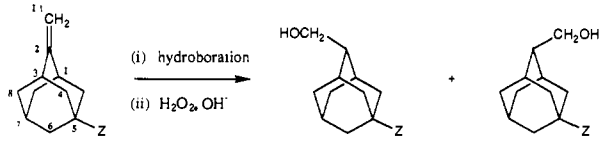
Table II. Catalyzed and Uncatalyzed Hydroborations of Alkenes **5**



5 *anti* *syn*

entry	Z	solvent	conditions	anti:syn
1	F	THF	catalyzed[a]	46:54
2	F	MePh	catalyzed	47:53
3	F	THF	uncatalyzed, BH_3[b]	63:37
4	F	MePh	uncatalyzed, BH_3	57:43
5	F	THF	uncatalyzed, 9-BBN[c]	68:32
6	F	THF	uncatalyzed, catecholborane[d]	65:35
7	Ph	THF	catalyzed	43:57
8	Ph	MePh	catalyzed	40:60
9	Ph	THF	uncatalyzed, BH_3	52:48
10	Ph	MePh	uncatalyzed, BH_3	53:47
11	$SiMe_3$	THF	catalyzed	75:25
12	$SiMe_3$	THF	uncatalyzed, BH_3	47:53

[a] Substrate:catecholborane = 1.0:1.5, 1 mol % of $[Rh(COD)Cl]_2$, 4 mol % of PPh_3, THF, −78 to 20 °C, 12 h. Throughout, product ratios determined via capillary GC of the silylated alcohols and checked via ^1H, ^{13}C, and, where appropriate, ^{19}F NMR. Stereochemistries assigned by correlation with le Noble's study of this reaction and subsequently via correlation of NMR data: see refs 19, 23, and 24. [b] Equimolar amounts of substrate and BH_3–THF, THF, 0–20 °C, 12 h. [c] Substrate: 9-BBN = 1.0:1.5, THF, 0–20 °C, 36 h. [d] Substrate:catecholborane = 1.0:8.0, THF, 70 °C, 2 h.

group are increased. Finally, competition experiments between acetate- and pivalate-protected allylic alcohol derivatives demonstrate that increased steric hindrance associated with the OX group can retard the rate of catalytic hydroborations, but the magnitude of that effect is small compared to the influence of electronic perturbations.

It is informative to correlate results obtained in these competition experiments with stereoselectivities in catalyzed hydroborations of the same substrates (vide supra). Syn:anti ratios observed in catalyzed hydroborations of butyl-substituted allylic alcohol derivatives **1** increase when acetate is substituted with trifluoroacetate and with pivalate. The competition experiments presented in Table I indicate that enhanced syn selectivities for the trifluoroacetate and pivalate are due to electronic and steric effects, respectively.

The 160–200-fold rate increase that accompanies changing acetate to trifluoroacetate in these competition experiments is most reasonably explained if complexation is the important step in the mechanism of catalyzed hydroborations (Scheme I). Allylic trifluoroacetates are better η^2-ligands than allylic acetates due to frontier-orbital arguments that parallel those outlined in Figure 1. If complexation of the alkene was irreversible, then rate enhancements for trifluoroacetates would follow from the frontier-orbital arguments outlined above. Conversely, if complexation of the rhodium is reversible, then enhancing the binding affinity of the alkene perturbs the net kinetic expression for the reaction by increasing the concentration of complexed alkene; rate acceleration then would be anticipated.

Hydroborations of 5-Substituted 2-Methyleneadamantanes (5)

Table II shows data collected for catalyzed and uncatalyzed hydroborations of alkenes **5**. The 5-substituents of these substrates are unlikely to have any steric influence on reactions at C^2; consequently 5-substituted adamantanes have been used to probe *electronic* effects in several different reaction types.[18-22] Electronic perturbations result from hyperconjugation, which lowers (X =

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(22) Xie, M.; le Noble, W. J. *J. Org. Chem.* **1989**, *54*, 3839.

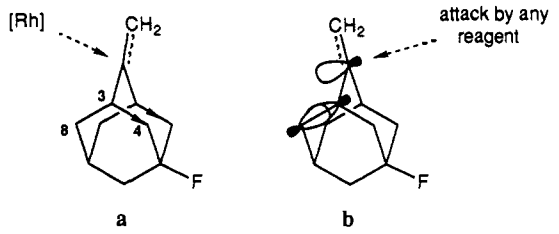


Figure 3. (a) Preferential approach in a rhodium-catalyzed hydroboration deduced by consideration of secondary orbital effects involving $d\pi-p\pi$ interactions. (b) Preferential approach of a hydroborating reagent as predicted using the Cieplak postulate.

F or Ph) or elevates (X = $SiMe_3$) the energy of the $C^{3,4}$ bonds relative to the $C^{3,8}$ linkages on the opposite face of the alkene; this in turn may cause π-facial selectivities in reactions at the alkene group. These selectivities are likely to be small, but they are significant provided they can be measured accurately.

In any event, stereoisomeric alcohols formed by hydroboration of alkenes **5** could not be separated by chromatographic techniques. Fortunately, selectivities for hydroboration of the fluoroalkene (**5**, X = F) were established by assigning the ^{13}C NMR spectra of the crude reaction mixtures and correlating these with product ratios measured by GC. The ^{13}C NMR assignments were made by (i) correlating our results with le Noble's BH_3 hydroboration of the same substrate,[19] (ii) deducing chemical shifts via the known[23] shielding effects of the pendant hydroxymethylene group on an adamantane skeleton, and (iii) assigning chemical shifts via the "additivity rule[24] for rigid structures". Coupling of the ^{19}F substituent to the carbons at C^4, but not to those at C^8, facilitated the assignment of ^{13}C NMR signals in this case. Shielding effects and the additivity rule were also used to unambiguously assign the ^{13}C NMR peaks of the phenyl-substituted (**5**, X = Ph) product. Unfortunately, the ^{13}C NMR chemical shifts for the C^4 and C^8 carbons of the silyl-substituted compounds were very close, so direct correlation of the ^{13}C NMR spectrum of the crude reaction mixture and the GC ratios was impossible. Consequently, the sense of the diastereoselection for the silicon-substituted compounds are assigned by inference, i.e. by assuming Cieplak selectivity in the uncatalyzed reaction.

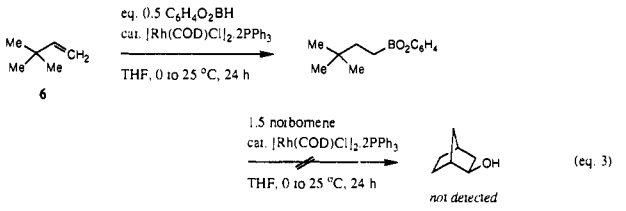
Results in Table II show catalyzed hydroborations of alkenes **5** occur preferentially on the alkene face opposite to σ-electron-withdrawing 5-substituents (giving excess syn product, entries 1, 2, 7, and 8), and on the same face as a σ-electron-releasing 5-substituent ($SiMe_3$, entry 11). Hyperconjugation lowers the energy of the σ^*-orbital of the C^3-C^4 bond relative to the C^3-C^8 bond when the C^5 substituent is electron-withdrawing (e.g. F or Ph, Figure 3a). Conversely, the σ^*-orbital of the C^3-C^4 bond is relatively high in energy when the 5-substituent is $SiMe_3$ (i.e. electron-releasing). Consequently, the catalyzed hydroborations shown in Table II occur preferentially on the face opposite the lowest lying σ^*-level, *in perfect accord with the hypothesis discussed above.*

5-Substituted methyleneadamantanes previously have been used[18-22] to test the "Cieplak postulate". Cieplak proposed[25,26] that attack of any reagent on an unsaturated center will be stabilized via overlap of the incipient σ^*-orbital with the highest energy σ-orbital of appropriate symmetry. Using this hypothesis, one would predict hydroborations of alkenes **5** would occur preferentially on the face anti to the *highest* available σ-orbital, i.e. syn to a σ-electron-withdrawing 5-substituent (e.g. Figure 3b) and anti to a σ-electron-releasing one.

Entry 2 in Table II confirms a result previously reported by le Noble and co-workers:[19] hydroboration of this alkene with BH_3 gives the anti product selectivity, just as one would predict from using the Cieplak postulate. In fact, selectivities for all of the uncatalyzed hydroborations presented in Table II are in accord with the model Cieplak described (entries 3–6, 9, 10, and 12). However, all of the rhodium-mediated hydroborations of the same substrates give opposite stereochemistry, *in contrast to the Cieplak postulate.* Notably, hydroboration of 5-fluoro-2-methyleneadamantane with a catecholborane/rhodium catalyst gives a 46:54 syn selectivity, whereas conventional hydroboration of the same substrate with catecholborane (no catalyst, higher temperature required) gives a 65:35 distribution in the opposite sense.

Computational studies have recently been cited as evidence that diastereofacial selectivities in other electronically perturbed alkenes can arise from solvation effects rather than the type of orbital interactions Cieplak proposes.[27] The selectivities observed in our work, however, do not appear to be particularly sensitive to solvent change from THF to MePh (entries 1 and 2, 3 and 4, 7 and 8, and 9 and 10); the uncatalyzed reactions are always selective in the sense predicted from the Cieplak postulate, and selectivities in the catalyzed reactions are opposite in every case. Solvent changes have been shown to have no effect in other tests of the Cieplak postulate.[28]

The Cieplak postulate was formulated to explain results in kinetically controlled reactions. It is not clear that rhodium-catalyzed hydroborations of substrates **5** are kinetically controlled, so it is premature to describe them as exceptions to the Cieplak postulate. Indeed, le Noble and Bodepudi have recently reported an apparent exception to the Cieplak hypothesis, which they explain in terms of thermodynamic control. In this work we have, however, accumulated evidence that overall the catalyzed hydroboration process is irreversible.[29] For instance, excess 3,3-dimethylbut-1-ene (**6**) was subjected to catalyzed hydroboration until all the available catecholborane was consumed (eq 3);



norbornene and more catalyst were added, and the mixture was stirred for an additional 24 h, oxidized, and analyzed by GC. Competition experiments show norbornene reacts twice as fast as 3,3-dimethylbut-1-ene (**6**) in catalyzed hydroborations; hence one would expect to observe norborneol at the end of this sequence if the catalyst reverses the hydroboration of **6**. In fact, no norborneol was detected, implying *the reductive elimination step in the catalyzed hydroboration of alkene* **6** *is irreversible.* In a second experiment (eq 4), 5-fluoro-2-methyleneadamantane (**5**) was hydroborated with excess $C_6H_4O_2BD$, and the products obtained after oxidation were analyzed via ^1H and ^2H NMR. No tertiary alcohol was detected, and almost all of the deuterium was located at the C^2 position of the adamantane skeleton; this implies that reversible formation of tertiary-rhodium alkyl complexes in these reactions is insignificant or does not occur at all. Others have suggested reversible formation of tertiary-alkyl rhodium complexes in these reactions;[30] such intermediates apparently are not formed in the catalyzed hydroboration of substrate **5** (X = F).

Conclusions

Results obtained in these two sets of experiments prove that *stereoselectivities and rates of catalyzed hydroborations of alkenes are sensitive to electronic effects in a manner that can be an-*

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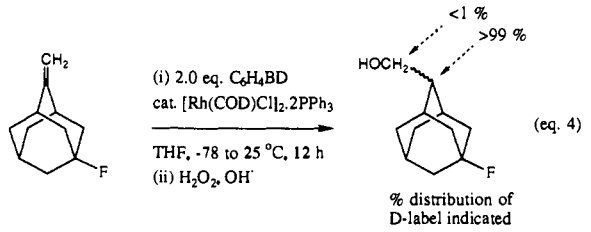

(eq. 4)

ticipated by assuming metal complexation is determinant, then considering secondary orbital interactions involving dπ–pπ interactions.[31] The theory we originally proposed to account for stereoselectivities in rhodium-catalyzed hydroborations of allylic alcohols **1** (and related substrates)[3-5,13] facilitates prediction of rate differences, and of stereoselectivities arising from very weak electronic perturbations.

Finally, Cieplak's postulate implies all kinetically controlled reactions of alkenes **5** should preferentially occur on the face syn to the best electron-withdrawing group (Figure 3b). Results presented in Table II for catalyzed hydroborations provide *a set of examples for which the Cieplak hypothesis is clearly not applicable.* If these catalyzed hydroborations are kinetically controlled, the stereoselectivities observed for substrates **5** are indicative of a fundamental flaw in the Cieplak postulate. Indeed, selectivities observed in reactions of the adamantane-based substrates that have been used to test the Cieplak postulate could be due to ground-state perturbation of the frontier orbitals involved; computational studies to explore this suggestion are in progress.

Experimental Section

General Procedures. Melting points were determined on a Mel-Temp or an Electrothermal digital capillary melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer 1600 series FTIR or on a Nicolet 205 FTIR. Low-resolution (EI) and high-resolution (EI) mass spectra were determined on a Finnigan 3300 mass spectrometer and a CAC 21/110 high-resolution mass spectrometer, respectively. GC was performed on a Shimadzu GC9A interfaced with an Apple Macintosh Plus using a 50-m (007 methyl phenyl (5%) silicone, 0.25-mm i.d., 0.25-μ film thickness) fused silica capillary column (Quadrex 007-2-50-0.25F). High-field NMR spectra were recorded on a Bruker AF300 (^{1}H at 300 MHz, ^{13}C at 75.4 MHz) or a Bruker AC250 (^{1}H at 250 MHz, ^{13}C at 62.9 MHz, and ^{19}F at 235 MHz). ^{2}H NMR spectra were recorded on a Bruker AMX-500 (^{2}H at 76.7 MHz). ^{1}H chemical shifts are reported in δ ppm relative to $CHCl_3$ (7.25 ppm), ^{13}C chemical shifts are reported in ppm relative to $CDCl_3$ (77.10 ppm for central peak), ^{19}F chemical shifts are reported in ppm relative to C_6F_6 (−163.0 ppm), and ^{2}H chemical shifts are reported relative to $CHCl_3$ (7.25 ppm) as internal standards. Thin-layer chromatography was performed on silica gel 60 F_{254} plates from Whatman. Flash chromatography was performed on SP silica gel 60 (230–400 mesh ASTM). Tetrahydrofuran and toluene were distilled from sodium benzophenone ketyl immediately before use. Borane–THF complex and 9-BBN solutions were purchased from Aldrich Chemical Co. and used as received. Catecholborane was purchased from Aldrich and distilled under reduced pressure before use. Organic solutions were dried over anhydrous magnesium sulfate. Trideuterioborane (BD_3) was purchased from Cambridge Isotope Laboratories, and deuteriocatecholborane was prepared according to literature procedures[32,33] and distilled under reduced pressure before use.

5-Hydroxy-2-methyleneadamantane (5, X = OH). To a stirred suspension of methyltriphenylphosphine iodide (17.8 g, 44 mmol) in THF was added 22 mL of a 2.01 M solution of *n*-BuLi in hexane at −78 °C. After 10 min 5-hydroxy-2-adamantanone[34] (3.0 g, 18 mmol) in 30 mL of THF was added to the clear red solution. The reaction mixture was allowed to warm to 20 °C and was stirred at this temperature for another 3 h. The solution was then diluted with diethyl ether (100 mL) and washed with water (2 × 100 mL) and saturated ammonium chloride solution (75 mL). The organic layer was dried and a crude yellow oil was obtained by removing the solvent under reduced pressure. Purification by flash chromatography (20% EtOAc in hexane) gave 2.24 g (75%) of a colorless crystalline solid: mp 112–113 °C; R_f 0.34 (EtOAc/hexane 20:80); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.65–1.80 (m, 10 H), 2.20 (m, 1 H), 2.64 (m, 2 H), 4.55 (s, 2 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 30.60 (C7), 38.20 (C8 + C10), 40.31 (C1 + C3), 44.96 (C6), 46.42 (C4 + C9), 68.05 (C5), 102.65 (C11), 155.38 (C2); IR ($CHBr_3$) 882 (s), 923 (s), 968 (s), 1065 (s), 1094 (s), 1109 (s), 1451 (m), 1657 (m), 2852 (s), 2915 (s), 3200–3500 (s br) cm^{-1}; MS (EI) *m/e* 165 (M + 1, 12), 107 (64), 95 (80), 91 (69), 29 (73), 27 (100); HRMS calcd for $C_{11}H_{16}O$ (M^+) 164.1201, found 164.1201.

5-Fluoro-2-methyleneadamantane (5, X = F). The procedure described here is considerably shorter than synthetic routes reported in the literature.[18,19] A 100-mL flask was charged with 5-hydroxy-2-methyleneadamantane (**5**, X = OH) (1.48 g, 9.0 mmol) and flushed with N_2; dichloromethane (30 mL) was added and the solution was cooled to −78 °C. (Diethylamido)sulfur trifluoride (1.62 g, 10.0 mmol) was added dropwise and the reaction mixture was allowed to warm to 20 °C. After stirring for 2 h, the reaction was quenched with water (1.0 mL) and diluted with diethyl ether (100 mL). The reaction mixture was washed with 1 M sodium bicarbonate (2 × 30 mL) and water (2 × 30 mL) and the organic layer was dried. Evaporation of the solvent under reduced pressure and purification by flash chromatography (hexane) gave 1.0 g (66%) of the pure product: R_f 0.52 (hexane); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.71 (m, 4 H), 1.93 (m, 6 H), 2.29 (m, 1 H), 2.71 (m, 2 H), 4.57 (s, 2 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 31.17 (d, $^3J_{CF}$ = 9.6, C7), 37.98 (C8 + C10), 40.55 (d, $^3J_{CF}$ = 10.2, C1 + C3), 42.35 (d, $^2J_{CF}$ = 17.2, C6), 43.57 (d, $^2J_{CF}$ = 17.5, C4 + C9), 91.34 (d, $^1J_{CF}$ = 184.6, C5), 103.38 (C11), 153.80 (C2); ^{19}F NMR (235 MHz, $CDCl_3$) δ −134.06 (m); HRMS calcd for $C_{11}H_{15}F$ (M^+) 166.1158, found 166.1158.

5-(Trimethylsilyl)-2-methyleneadamantane (5, X = SiMe$_3$). A 100-mL flask was charged with 1.8 g (4.5 mmol) of iodomethyltriphenylphosphorane and flushed with N_2; THF (50 mL) was added and the mixture was cooled to −78 °C. After 5 min *n*-BuLi (2.0 mL of 2.01 M in hexanes) was added and the white suspension turned clear red. 5-(Trimethylsilyl)adamantan-2-one[21] (0.5 g, 2.2 mmol) in 10 mL of THF was added and the solution was allowed to warm to 20 °C. After stirring for 2 h, the reaction mixture was diluted with diethyl ether (100 mL) and washed with water (2 × 40 mL). The organic layer was dried and 200 mg of crude product was obtained after the solvent was removed under reduced pressure. Purification by flash chromatography (hexane) yielded 100 mg (20%) of the product as a yellow oil, which was 85–90% pure by capillary GC analysis: R_f 0.95 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.11 (s, 9 H), 1.69–1.89 (m, 11 H), 2.47 (m, 2 H), 4.53 (s, 2 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ −5.36 ($SiMe_3$), 21.55 (C5), 27.78 (C7), 36.82 (C4 + C9), 38.82 (C1 + C3), 39.59 (C8 + C10), 40.93 (C6), 102.51 (C11), 158.73 (C2); HRMS calcd for $C_{14}H_{24}Si$ (M^+) 220.1647, found 220.1646.

5-Phenyl-2-methyleneadamantane (5, X = Ph). A 250-mL round-bottom flask was charged with 1.95 g of zinc powder (29 mmol) and flushed with Ar; THF (10 mL) was added followed by 4.4 g (16.5 mmol) of diiodomethane in dichloromethane (10 mL). The gray slurry was cooled to 0 °C and, after stirring for 30 min, 0.36 mL (1.5 mmol) of neat titanium tetrachloride was added. After 30 min 0.50 g (2.2 mmol) of 5-phenyladamantan-2-one[34] in THF (5 mL) was added, the reaction mixture was allowed to warm to 20 °C, and was stirred overnight. The solution was then diluted with hexane (150 mL), filtered through Celite, and washed with 1 M sodium bicarbonate solution (3 × 40 mL) and water (2 × 50 mL). The organic layer was dried and the crude product was obtained as a dark brown oil. The crude material was dissolved in diethyl ether (50 mL) and filtered over alumina (activity I). After the solvent was removed under reduced pressure, 0.36 g (73%) of pure title

(31) The stereoselectivity and rate data are mutually consistent with this hypothesis. For instance, Table II shows face selectivities are small in catalyzed hydroborations of systems with electron-withdrawing 5-substituents (entries 1 and 5), but greater selectivity is observed for the trimethylsilyl-substituted system (entry 7). Exactly the opposite trend is observed for the uncatalyzed reactions; it is the electron-releasing silyl-substituent that confers *least* selectivity (entries 2, 6, and 8). These observations are consistent with *rate acceleration* for catalyzed hydroborations of the adamantane systems when substituted with electron-withdrawing groups leading to *decreased stereoselectivity*, whereas *rate retardation* results for the relatively electron-rich 5-trimethylsilyl-substituted alkene, and *increased selectivity* results. The reverse considerations can be used to explain observations in the uncatalyzed series. Similar considerations should apply to the allylic alcohol substrates **1**, but for those substrates the allylic acetates react with less selectivity than the allylic trifluoroacetates. We suspect the allylic trifluoroacetates react with higher selectivity because stereoelectronic effects favor one particular reactive conformation, and the reaction occurs relatively rapid from that conformation. Conversely, the allylic acetates have less population of molecules in the corresponding reactive conformation, and the reaction occurs more slowly from this conformer. For adamantanes prior alignment in a given reactive conformation is not an issue.

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compound was obtained as a colorless oil, which solidified upon cooling: mp 36–37 °C; R_f 0.6 (hexane); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.91 (m, 4 H), 2.06 (m, 6 H), 2.20 (m, 1 H), 2.70 (m, 2 H), 4.64 (s, 2 H), 7.37 (m, 5 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 28.97 (C7), 36.47 (C5), 38.80 (C8 + C10), 39.36 (C1 + C3), 42.74 (C6), 44.99 (C4 + C9), 101.53 (C11), 124.94 (arom CH), 125.74 (arom CH), 128.22 (arom CH), 150.22 (arom C), 156.97 (C2); IR ($CHBr_3$) 758 (s), 888 (s), 1019 (m), 1440 (s), 1495 (s), 1600 (w), 1651 (s), 2850 (s), 2915 (s), 2977 (s), 3065 (s) cm^{-1}; MS (EI) *m/e* 224 (M^+ 100); HRMS calcd for $C_{17}H_{20}$ (M^+) 224.1565, found 224.1565.

General Procedure for Catalyzed Hydroborations. A Schlenk tube charged with a catalytic amount of 2.4 mg (0.005 mmol, 1%) of $[Rh(COD)Cl]_2$ and 5.2 mg (0.02, 4%) of triphenylphosphine was three times evacuated/flushed with N_2. Toluene or THF (2 mL) was added followed by 0.5 mmol of the substrate in the same solvent (2 mL). The bright yellow solution was cooled to −78 °C and 120 mg (1 mmol, 2 equiv) of catecholborane in THF or toluene (1 mL) was added. The reaction mixture was allowed to warm to 20 °C and stirred at this temperature for 12 h. Ethanol (1 mL) was added at 0 °C followed by 1.7 mL of 3 M NaOH solution and 1 mL of 30% H_2O_2. The mixture was stirred for 6 h at 20 °C and was then diluted with 10 mL of 1 M NaOH solution. Extraction with diethyl ether (3 × 75 mL), washing of the combined organic fractions with 1 M NaOH solution (50 mL), water (50 mL), and saturated NaCl solution (50 mL), and evaporation of the solvent under reduced pressure after drying provided the crude product. Small portions (typically 5 mg) of the crude mixture were reacted with trimethylsilyl chloride (0.05 mL) and hexamethyldisilazane (0.15 mL) in pyridine[35] and the white suspension was analyzed by GC to determine the ratios of isomeric trimethylsilyl ethers.

General Procedure for Uncatalyzed Hydroborations. To a solution of 0.5 mmol of substrate in THF or toluene (10 mL) was added 0.5 mL of 1.0 M BH_3–THF complex at 0 °C. The reaction mixture was allowed to warm to 20 °C and was stirred at this temperature for 6 h. Oxidation and workup were carried out as described above for catalyzed hydroboration.

Catalyzed and Uncatalyzed (BH_3) Hydroborations of 5 (X = F). The crude mixture of stereoisomers was obtained following the procedures described above for the catalyzed and uncatalyzed reactions. Yields for reactions carried out in THF after purification by flash chromatography (20% EtOAc in hexane): catalyzed 68%, uncatalyzed 75%. Ratios syn:anti for trimethylsilyl ether derivatives determined by GC were catalyzed 54:46 and uncatalyzed (BH_3) 37:63: R_f 0.25 (EtOAc/hexane 20:80); ^{1}H NMR (250 MHz, $CDCl_3$, data for mixture of isomers throughout) δ 1.51–2.17 (m, 14 H), 3.66 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, syn isomer), 3.70 (d, $^3J_{HH}$ = 7.4 Hz, 2 H, anti isomer); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 30.31 (C8 + C10, anti), 31.09 (d, $^3J_{CF}$ = 8.8, C7), 31.57 (d, $^3J_{CF}$ = 10.5, C7), 32.46 (d, $^3J_{CF}$ = 10.1, C1 + C3), 32.61 (d, $^3J_{CF}$ = 9.4, C1 + C3), 37.04 (C8 + C10, syn), 37.44 (d, $^2J_{CF}$ = 17.5, C4 + C9, syn), 43.14 (d, $^2J_{CF}$ = 20.3, C6), 43.53 (d, $^2J_{CF}$ = 17.7, C4 + C9, anti), 45.48/45.70 (C2), 64.11/64.37 (C11), 92.59 (d, $^1J_{CF}$ = 183, C5); ^{19}F NMR (235 MHz, $CDCl_3$) δ −132.42 (m, 1, syn), −129.77 (m, 1, anti); IR ($CHBr_3$) 904 (m), 939 (m), 952 (m), 999 (m), 1039 (s), 1057 (s), 1104 (s), 1354 (m), 1455 (m), 2861 (s), 2925 (s), 3379 (s br), 3597 (m br) cm^{-1}; MS (EI) *m/e* 184 (M^+, 7), 166 (100), 153 (47), 91 (27); HRMS calcd for $C_{11}H_{17}OF$ (M^+) 184.1263, found 184.1263.

Hydroboration of 5 (X = F) with 9-BBN. 5-Fluoro-2-methyleneadamantane (100 mg, 0.6 mmol) was placed in a 50-mL flask, flushed with N_2, dissolved in THF (6 mL), and the solution was cooled to −78 °C. Then 1.0 mL of 0.5 M 9-BBN solution in THF was added and the solution was stirred for 36 h at 20 °C. Oxidation and workup were carried out as described previously under catalyzed hydroborations. Yield: 74 mg (67%). The syn:anti ratio of trimethylsilyl ether derivatives determined by GC was 32:68.

Hydroboration of 5 (X = F) with Catecholborane at 70 °C. A 50-mL flask equipped with a reflux condenser was charged with 50 mg (0.3 mmol) of compound **5** , (X = F) under N_2; THF (6 mL) was added followed by 0.3 mL (8 equiv) of catecholborane. The reaction mixture was heated at reflux with stirring for 2 h. Oxidation and workup were carried out as described under the general procedure for catalyzed hydroborations. The syn:anti ratio of trimethylsilyl derivatives determined by GC was 35:65.

Catalyzed and Uncatalyzed Hydroboration of 5 (X = $SiMe_3$). For procedures, see the general procedures for catalyzed and uncatalyzed hydroborations. The yields after purification by flash chromatography (hexane): catalyzed 66%, uncatalyzed 93%. The ratios of syn:anti trimethylsilyl ethers determined by GC were catalyzed 25:75 and uncatalyzed 53:47: R_f 0.40 (EtOAc/hexane 15:85); ^{1}H NMR (300 MHz, $CDCl_3$, data for mixture of isomers throughout) δ −0.14 (s, 9 H), 1.38–1.86 (m, 14 H), 3.70 (m, 2 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 20.73/21.31 (C5), 27.44/27.84 (C7), 28.65/28.77 (C1 + C3), 31.25, 31.94, 37.64, 38.56, 38.91, 46.88/47.11 (C2), 64.95/65.06 (C11); HRMS calcd for $C_{14}H_{26}OSi$ (M^+) 238.1753, found 238.1753.

GC analysis of the silylated crude mixtures of the catalyzed and uncatalyzed hydroborations showed the presence of two contaminants, which could be isolated by careful flash chromatography (5–10% EtOAc in hexane). Spectral analysis and mass spectroscopy data showed that the contaminants consisted of the syn and anti isomers of 2-(hydroxymethyl)-5-(pentamethyldisilyl)adamantane (ratios from GC analysis: catalyzed 20:80, uncatalyzed 54:46). It was determined that these products originated from the corresponding alkene **5** (X = $SiMe_2SiMe_3$), which was present as an impurity in the starting material for the hydroborations. Data for isolated material (one isomer): ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.08 (s, 6 H), 0.04 (s, 9 H), 1.42–1.85 (m, 14 H), 3.67–3.72 (m, 2 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ −6.47 ($SiMe_2$), −0.72 ($SiMe_3$), 22.39, 28.04, 28.88, 32.73, 38.89, 39.08, 46.96, 65.06; MS (EI) M^+ 296 (26), $M^+ - SiMe_3$ 223 (77); HRMS calcd for $C_{16}H_{32}OSi_2$ (M^+) 296.1992, found 296.1991.

Catalyzed and Uncatalyzed Hydroboration of 5 (X = Ph). For procedures see the general procedures for catalyzed and uncatalyzed hydroborations. The yields for reactions carried out in THF after purification by flash chromatography (20% EtOAc in hexane) were catalyzed 88% and uncatalyzed 96%. The syn:anti ratios of alcohols determined by GC were catalyzed 57:43 and uncatalyzed 48:52: mp 59–60 °C; R_f 0.35 (EtOAc/hexane 15:85); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.58–2.08 (m, 14 H), 3.74 (d, $^3J_{HH}$ = 7.3 Hz, 2 H, anti), 3.80 (d, $^3J_{HH}$ = 7.3 Hz, 2 H, syn); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 29.06/28.60 (C7), 29.80/29.96 (C1 + C3), 31.08 (C8 + C10, anti), 36.03/36.47 (C5), 37.32 (C4 + C9, syn), 37.98 (C8 + C10, syn), 43.69/43.92 (C6), 44.32 (C4 + C9, anti), 45.87/46.09 (C2), 64.65/64.70 (CH_2OH), 124.72/124.86 (arom CH), 125.65 (arom CH), 129.15 (arom CH), 150.65/150.83 (arom C); IR ($CHBr_3$) 755 (s), 1007 (s), 1022 (m), 1068 (m), 1445 (m), 1451 (m), 1466 (m), 1600 (w), 2852 (s), 2919 (s), 3025 (s), 3300–3550 (s br) cm^{-1}; MS (EI) *m/e* M^+ 242 (87), 211 (31), 155 (100), 91 (67); HRMS calcd for $C_{17}H_{22}O$ (M^+) 242.1671, found 242.1672.

General Procedure for Competition Experiments. A Schlenk tube charged with 2.5 mg (0.005 mmol) of $[Rh(COD)Cl]_2$ and 5.2 mg (0.02 mmol) of triphenylphosphine was evacuated/flushed three times with N_2. The mixture was dissolved in THF (1 mL), and 1.0 mmol of each alkene in 4 mL of THF was added. The solution was stirred at 20 °C for 10 min and 6 mg of catecholborane in 0.5 mL of THF was added. The reaction mixture was stirred for 12 h and then 1 mL of ethanol was added at 0 °C, followed by 1.5 mL of 1 M NaOH solution and 0.7 mL of 30% H_2O_2. After stirring for 6 h, the mixture was diluted with 50 mL of diethyl ether and washed with 1 M NaOH solution (2 × 10 mL). Acetonides of the crude diols were formed by adding 2,2-dimethoxypropane (5 equiv) and a catalytic amount of *p*-toluenesulfonic acid; the mixture was stirred for 12 h and washed with 10 mL of saturated aqueous sodium bicarbonate. The ratios of the different actonides were determined by calibrated GC.

Catalyzed Hydroboration of 5 (X = F) with Deuteriocatecholborane. Procedure as described above: R_f 0.25 (20% EtOAc in hexane); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.64–2.19 (m, 13 H), 3.64 (s, 2 H, syn), 3.68 (s, 2 H, anti); ^{13}C NMR (62.90 MHz, $CDCl_3$) δ 45.60 (m, CD); ^{2}H NMR (76.7 MHz, $CHCl_3$) δ 1.72 (syn), 1.78 (anti); HRMS calcd for $C_{11}H_{16}OFD$ (M^+) 185.1326, found 185.1326.

Catalyzed Hydroboration of 3,3-Dimethyl-1-butene. A Schlenk tube charged with 2.5 mg (0.005 mmol, 1%) of $[Rh(COD)Cl]_2$ and 5.2 mg (0.02 mmol, 2%) of triphenylphosphine was evacuated/flushed three times with Ar; THF (2 mL) was added followed by 168 mg (2 mmol) of 3,3-dimethyl-1-butene. The solution was cooled to 0 °C, 120 mg (1 mmol, 0.5 equiv) of catecholborane was added in THF (1 mL), and the solution was allowed to warm to 20 °C. After the solution was stirred for 12 h, 282 mg (3 mmol) of norbornene was added with another 2.5 mg of $[Rh(COD)Cl]_2$ and 5.2 mg of triphenylphosphine in THF (2 mL). The resulting solution was stirred at 20 °C for 24 h. Oxidation of the alkylboron species present in the reaction mixture and subsequent workup were carried out as described under the general procedure for catalyzed hydroboration. GC analysis of the crude material showed the absence of the hydroboration product of norbornene.

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