Transition-Metal-Promoted Hydroborations of Alkenes, Emerging Methodology for Organic Transformations

KEVIN BURGESS* and MICHAEL J. OHLMEYER

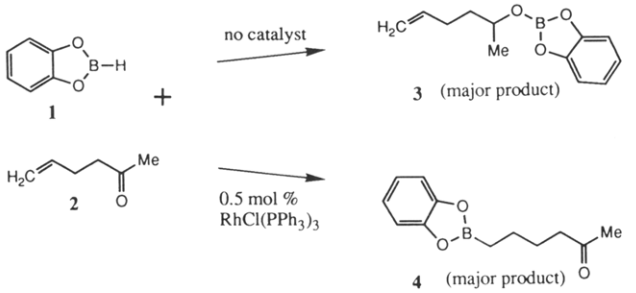
Chemistry, Rice University, Box 1892, Houston, Texas 77251

Received January 31, 1991 (Revised Manuscript Received May 14, 1991)

Contents

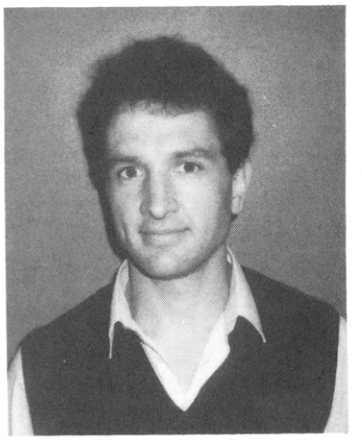
I. Introduction

Additions of catecholborane to alkenes are generally very slow at room temperature, but they can be greatly accelerated by small amounts of transition-metal complexes. There are several ways such "catalyzed hydroborations" may prove to be valuable in organic syntheses. Catalysis can alter the *chemoselectivity* of reactions of multifunctional substrates; for instance, without catalyst catecholborane **1** adds to the carbonyl group of ketone **2**, whereas hydroboration of the alkene takes place preferentially in the presence of less than 1 mol % of $RhCl(PPh_3)_3$.[1] Catalysis also provides



alternatives for manipulating regio-, stereo-, and chemoselectivity in hydroboration processes.

Almost all studies of the potential of transition-metal-mediated hydroborations in organic syntheses have focused on catecholborane/rhodium(+1) catalysts, but other systems are also discussed in this review, to indicate how the field may develop.



Kevin Burgess was born in London, England in 1958. He received his B.Sc. from Bath University and worked with A. R. Katritzky for a masters degree from The University of East Anglia. In 1980 he joined Jack Lewis' research group at Cambridge University and studied trisosmium cluster chemistry until graduating in 1983. As a postdoctoral associate at The University of Wisconsin with Barry M. Trost, Kevin Burgess became involved with organometallic catalysis, an interest he pursued independently back in Cambridge, England for a few years after that. In 1987 he became an assistant professor at Rice University. His current interests focus upon new methodology for asymmetric syntheses, including uses of transition-metal complexes, enzymes, and chiral-directing groups. In the long-term he plans to apply these efforts to peptide and carbohydrate chemistry.

In 1965 Michael J. Ohlmeyer was born in London, although he has spent most of his life so far in Northern Ireland. He graduated from Cambridge University in 1986, joined the chemistry graduate program at Rice University, and became the first Ph.D. student to graduate from the Burgess group. Michael Ohlmeyer is currently a postdoctoral associate with Clark Still at Columbia.

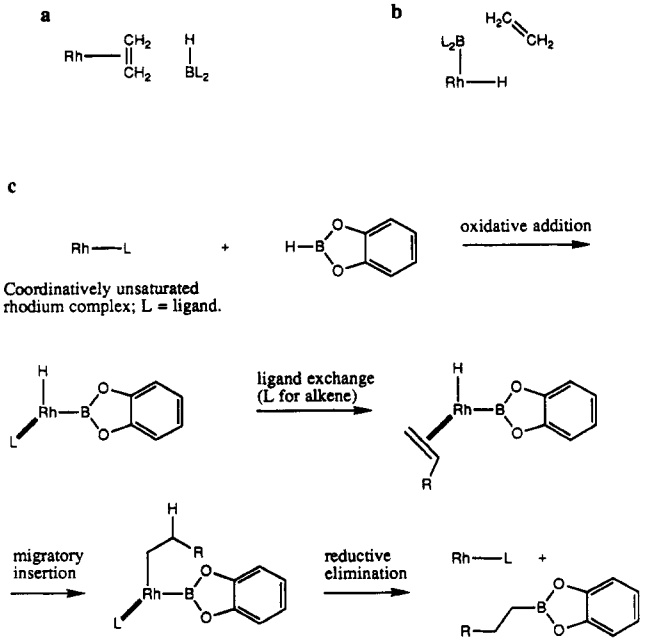
II. Mechanistic Considerations

A. Rhodium-Mediated Hydroborations with Catecholborane

The mechanism(s) of rhodium-catalyzed hydroboration reactions remains to be established, but they are certainly fundamentally different from the corresponding uncatalyzed processes.[2-4] Transient coordination of alkenes and attack of a free boron hydride on the opposite π-face (Scheme Ia) is probably not involved

0009-2665/91/0791-1179$09.50/0

SCHEME I. Conceivable Mechanisms for Rhodium-Mediated Hydroboration Reactions[a]

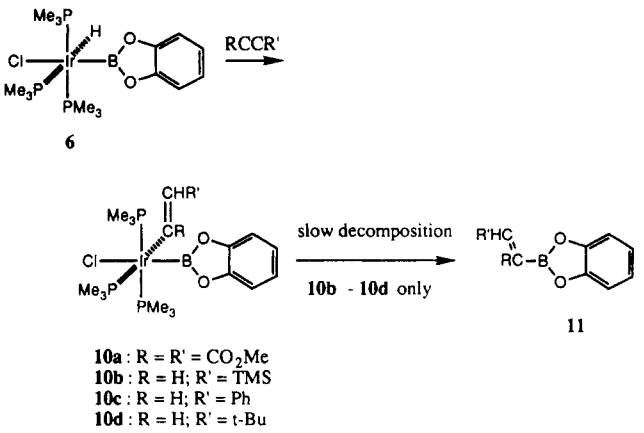


[a] (a) Unfavorable electrophilic attack of catecholborane on a coordinated alkene. (b) Unfavorable nucleophilic attack of an alkene on a hydridoborylrhodium complex. (c) Plausible mechanism involving activation of the alkene and the boron hydride by the metal.

because η^2-coordination *deactivates* alkenes toward electrophilic attack. Conversely, oxidative addition of a boron hydride renders the boron atom *less* electron deficient due to donation from metal d orbitals hence borylrhodium complexes, likely intermediates in the catalytic cycle, are not disposed to additions of free alkenes as indicated in Scheme Ib. One may conclude that both the boron hydride and the alkene probably become tethered to the metal in the course of rhodium-catalyzed hydroborations. A generalized mechanism for Rh-promoted hydroborations[1] is depicted in Scheme Ic.

The first step in Scheme Ic is consistent with numerous reports implicating oxidative additions of B–H bonds to coordinatively unsaturated metal centers.[5-13] Particularly significant among these are oxidative additions of catecholborane (eq 1)[14] and of 9-BBN (eq 2, 9-BBN = 9-borabicyclo[3.3.1]nonane),[15] to iridium(+1) complexes **5** and **7**, respectively. The most pertinent observation, however, is that Wilkinson's catalyst (**8**) reacts with stoichiometric amounts of catecholborane to give complex **9**;[16] isolated samples of this material react with alkenes to give hydroboration products (eq 3).[1] An analogue of **9** [$RhHCl(P^iPr_3)_2(BO_2C_6H_4)$] has been characterized via single-crystal X-ray diffraction studies.[17]

The second step in the postulated mechanism for rhodium-promoted hydroboration of alkenes by catecholborane, is alkene binding followed by migratory insertion of the alkene into the rhodium hydride bond. Although this process has not been extensively studied for boron-containing complexes, there is ample precedent from studies of other compounds. So far, the best parallel is insertion of *alkynes* into the Ir–B bond of the boryliridium complex **6**.[14] The vinyl complexes so formed (**10**) are stable if substituted with two electron-withdrawing substituents (R and R′), otherwise reductive elimination occurs to give vinylboronates **11**; the latter reaction mimics the final step in the postulated mechanism for rhodium-mediated hydroborations.

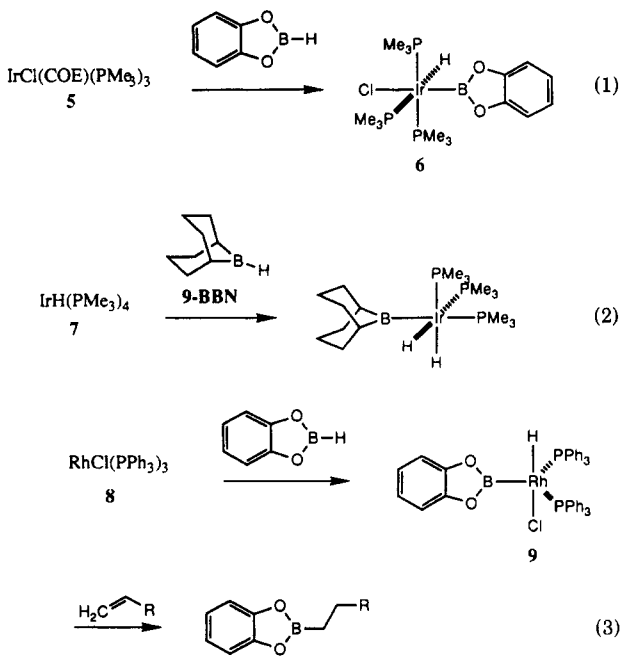


10a: R = R′ = CO_2Me
10b: R = H; R′ = TMS
10c: R = H; R′ = Ph
10d: R = H; R′ = t-Bu

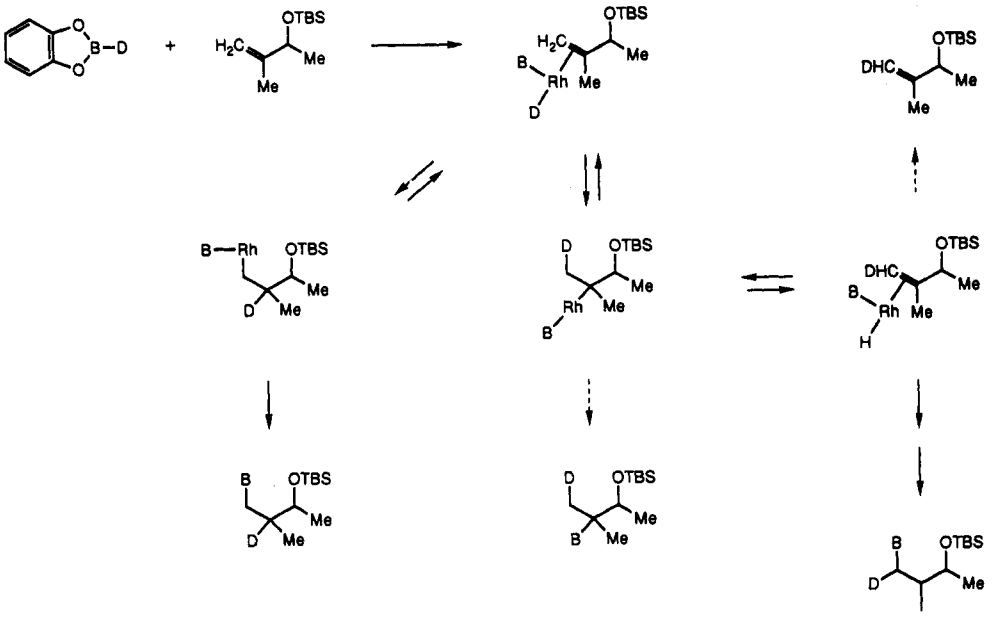
Complex **6** is a catalyst for hydroborations of alkynes with catecholborane (6 turnovers in 2 days). Investigations of this system by NMR revealed that complexes **10** are the "resting state" in the catalytic cycle, implying reductive elimination is the slow step in the overall transformation.

Alternatives to the generalized mechanism discussed above are possible (although less plausible). For instance, it is conceivable that for certain substrate types, reaction proceeds via insertion into rhodium–boron, rather than into the rhodium–hydride bonds. For terminal alkenes however, this would require formation of a (sterically unfavorable) secondary alkyl complex to account for the overall regiochemistry of the hydroboration.

The reaction pathway shown in Scheme Ic is presented in very general terms because no information is available regarding the precise nature of the complexes involved, relative rates/reversibility of the steps, and



SCHEME II. Published Rationale for Deuterium Incorporation

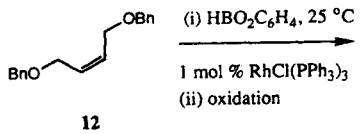


other important parameters. Indeed, the mechanism(s) of Rh-catalyzed hydroborations may remain obscure for some considerable time, and even if convincing mechanistic data were available for one particular system, it would not necessarily be applicable to other functionalized organic substrates, hydroborating reagents, and catalysts. Furthermore, catalyzed hydroborations are complicated by side reactions which can skew the results of mechanistic studies. For instance, the reaction of catecholborane with $RhCl(PPh_3)_3$[17-19] affords $RhClH_2(PPh_3)_3$, $RhH(PPh_3)_3$, catecholborane disproportionation products, phosphine–borane adducts, and other unidentified materials, any of which could have a bearing on the outcome of hydroborations mediated by this system.[19] This is evident from deuterium-labeling studies outlined below.

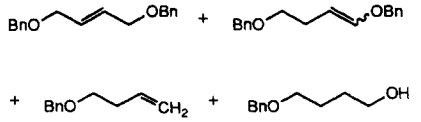
Rhodium complexes also accelerate additions of catecholborane to β-hydroxyketones,[20] but it is not clear that these reactions are mechanistically related to catalyzed hydroborations of alkenes.

1. Side Reactions that Compete with Rh-Catalyzed Hydroborations

Catalyzed hydroborations of some substrates can be complicated by side reactions arising from β-elimination processes. For example, Rh-mediated hydroboration of (*Z*)-1,4-bis(benzyloxy)but-2-ene (**12**) affords products

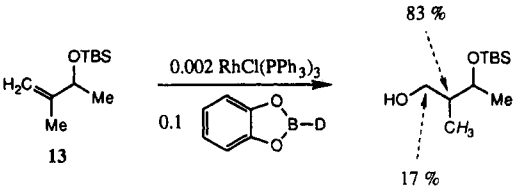


12



corresponding to double-bond isomerization, and elimination of benzyloxy groups/hydroboration of the resulting alkenes.[21] Similarly, rhodium-catalyzed hydroboration of (*Z*)-stilbene is accompanied by isomerization to the *E* isomer.[18] In other cases, significant amounts of hydrogenation products have been observed.[18,22]

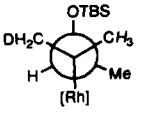
Two studies of catalyzed hydroborations with deuterocatecholborane 1-D_1 have been performed. The first[23] suggested catalyzed hydroboration of 2-methyl-3-[(*tert*-butyldimethylsilyl)oxy]but-1-ene (**13**) with deuterocatecholborane gives significant label (17%) at the hydroxymethylene terminus of the product. To



13

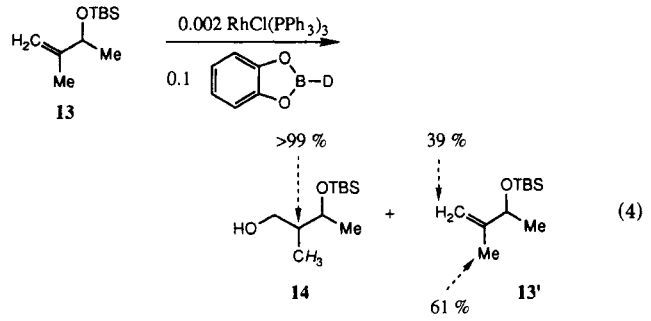
% D distribution as indicated
no D detected in recovered **13**

rationalize this result it was proposed that an intermediate rhodium–alkene complex undergoes reversible migratory insertion affording a significant amount of a tertiary alkyl–rhodium complex. Further, it was suggested that this did not undergo reductive elimination (no tertiary alcohol was observed after oxidation) but instead gave 100% stereoselective β-hydride elimination with the DH_2C group (see Newman projection I, 0% β-hydride elimination with the diastereotopic CH_3 group) to regenerate a rhodium alkene complex labeled at the alkene terminus. This hypothesis is outlined in Scheme II.



I

Results from the second study do not agree with the first; they indicate reaction of substrate **13** with deuterocatecholborane ($C_6H_4O_2BD$) in the presence of catalytic $RhCl(PPh_3)_3$ or $[Rh(COD)Cl]_2{\cdot}4PPh_3$, followed by oxidation, gives alcohol **14** *labeled almost exclusively at C*[2]. A very small amount of the total deuterium is detected in recovered starting material **13'** if the reaction is run with use of only 0.1 equiv of $C_6H_4O_2BD$, as indicated in eq 4. Moreover, the deuterium that is

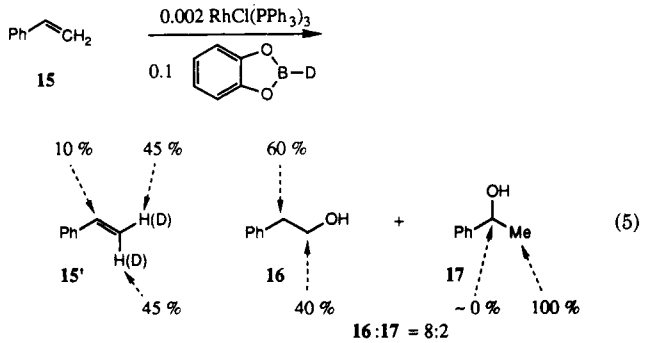


(4)

>98 % of total D detected in **14**, <2 % in **13'**

incorporated into the recovered starting material is distributed in a near statistical consistency with *diastereorandom* β-elimination from a tertiary alkyl intermediate of type I. These data indicate minimal involvement of tertiary rhodium–alkyl intermediates, presumably because formation of primary metal–alkyls are strongly favored in migratory insertion reactions involving 1,1-disubstituted alkenes. Also the fact that no tertiary alcohol is detected implies strongly that any tertiary rhodium–alkyl species formed *is not* an intermediate in, or connected with the catalytic cycle.

Additions of (D)H–Rh to monosubstituted alkenes are, predictably, less regioselective than for additions to alkene **13**, as illustrated by the wide distribution of deuterium indicated in eqs 5 and 6; double-bond isomerization in the experiment involving 1-decene (eq 6) underlines this point. There are minor discrepancies between the first[23] and second deuterium-labeling studies; results from the latter work[24] are shown below.

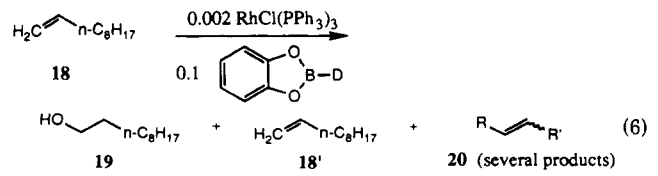


(5)

% of total D, **15'**:**16**:**17** = 40:46:14

High-resolution mass spectroscopy indicates some molecules of products **15'**, **16**, and **17** have more than one deuterium atom per molecule, indicative of insertion/reductive elimination reactions involving D–Rh before the hydroboration event.

It is not possible to differentiate between hydride migration processes mediated by intermediates in the catalytic hydroboration cycle, and those promoted by extraneous hydridorhodium complexes which form when catecholborane is mixed with $RhCl(PPh_3)_3$. Un-



(6)

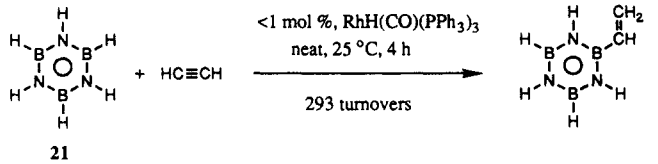
deuterium observed in all possible C D positions in **19**, **18'**, and **20**

published work[17,19] indicates that over 50% of the rhodium atoms form $H_2RhCl(PPh_3)_3$ when catecholborane is mixed with $RhCl(PPh_3)_3$, and traces of $HRh(PPh)_3$ also form. These hydrido complexes are probably not directly involved in the catalytic cycle for hydroboration, but would be capable of double-bond isomerization reactions *and distributing deuterium labels.*[25,26] Consequently, deuterium-labeling studies of the type outlined above reveal little about the mechanism of rhodium-mediated hydroborations.

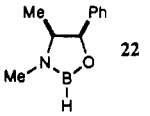
B. Other Systems for Catalyzed Hydroborations

Catalyzed hydroborations are not restricted to rhodium complexes and catecholborane. Indeed, this whole area evolved from studies of boron hydride clusters/alkenes (or alkynes) in the presence of several different transition metals.[5-11] Pyrophoric and relatively inaccessible boron cluster compounds, however, are not convenient reagents for organic chemistry.

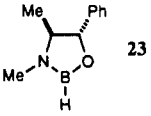
Borazine **21** also undergoes some hydroboration reactions in the presence of transition-metal catalysts.[12,13]



This boron hydride is commercially available, but so expensive that it is unlikely to be used in organic syntheses. Compounds **22** and **23**, however, are amenable to transition-metal-promoted hydroborations, and are easily prepared from inexpensive materials; they have been screened as possible reagents for enantioselective hydroborations (vide infra), but their behavior in other catalyzed hydroborations remains to be explored.



22

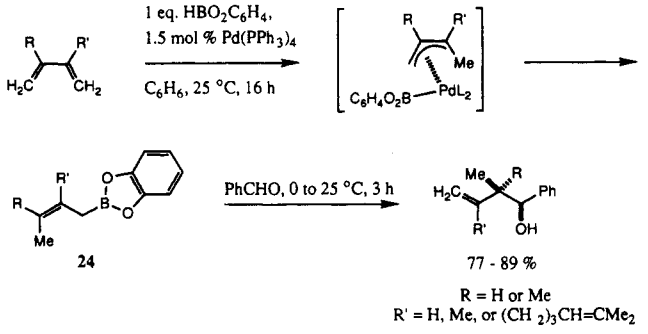


23

Besides $RhCl(PPh_3)_3$ and $[RhCl(COD)]_2$/phosphine mixtures, complexes which have been reported to promote synthetically useful hydroboration reactions include $[RhCl(COD)]_2$, $RhCl(CO)\{(PPh_3)_3\}_2$, $RhCl(CO)\{(AsPh_3)_3\}_2$, and, less active, $HRuCl(CO)\{(PPh_3)_3\}_3$.[1]

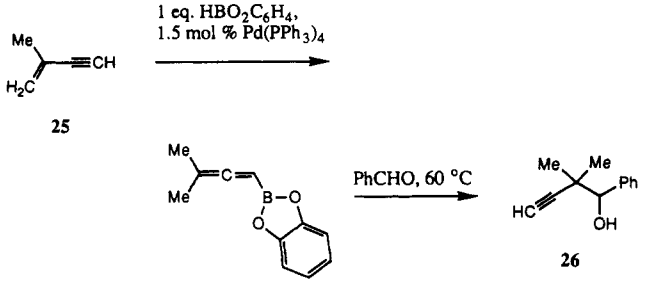
One report[1] stated, "...complexes of platinum, palladium, iridium, and cobalt exhibit no or only minor catalytic effects". Unfortunately, the substrates and conditions for the screening reactions in question were not given, and this statement is not universally accurate. For instance, subsequent work has demonstrated $Pd(PPh_3)_4$ is a catalyst for hydroboration of dienes.[27] This reaction may proceed via π-allyl complexes which undergo reductive elimination to give (*Z*)-allylic boronates

(e.g. 24), products which are conveniently trapped by reactions with aldehydes. Similarly, conjugated enyne



24

25 gives an allenic boronate under these conditions, which affords homopropargylic alcohol 26 on reaction with benzaldehyde. Rhodium complexes were reported



25 26

to be poor catalysts for these same transformations, but they *do* promote hydroborations of 1,3-cyclohexadiene by catecholborane; $Rh_4(CO)_{12}$ (mol % not specified) is apparently a relatively active catalyst.[27]

Finally, three reports[28-30] describe catalytic hydroborations of alkenes mediated by $BH_4^-/TiCl_3$ or $BH_4^-/TiCp_2Cl_2$. In each of these reactions the catalyst is preformed via reaction of the Ti complex and borohydride, usually at 25 °C, before the substrate is introduced.

Borohydride and $TiCp_2Cl_2$ are known to react at room temperature according to the following equation:[31]

$$2TiCp_2Cl_2 + 4BH_4^- = 2TiCp_2(BH_4) + B_2H_6 + H_2 \quad (7)$$

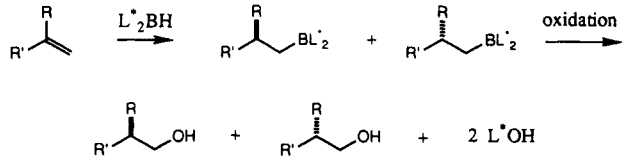
In many of the reported[28-30] "Ti-catalyzed hydroborations" almost 20 mol % of titanium complex and 1 equiv of borohydride are used; this would produce a significant amount of diborane which is apparently not removed before addition of the substrate. Furthermore, if $TiCp_2(BH_4)$ were to react at all four B–H bonds, 20 mol % of "catalyst" could give a maximum theoretical yield of 80% in one turnover. It seems likely that some hydroboration products in these reactions arise from adventitious diborane formed via the eq 7, and/or via transformations of BH_4^- wherein titanium complexes simply act as a Lewis acid. In other examples, however, only 5 mol % of titanium complex is used, and the catalytic role of this material seems more certain. Nevertheless, we prefer to describe these reactions as "metal promoted", rather than "metal catalyzed" until further studies have been performed to elucidate the role of titanium complexes in these transformations.

Titanium-mediated hydroborations could involve π-complexes similar to those which have been observed in analogous hydroalumination reactions,[32] but further research is required to establish this.

III. Enantioselectivity

Established methods for asymmetric hydroboration of prochiral alkenes rely on reagent-controlled diastereoselectivity, i.e. optically active borane is used to induce handedness in the substrate.[33] For instance, diisopinocampheylborane (Ipc_2BH) reacts with many *Z*-alkenes to give boranes of one diastereomeric series in preference to the other; these can be converted to enantiomerically enriched alcohols via oxidation.[34]

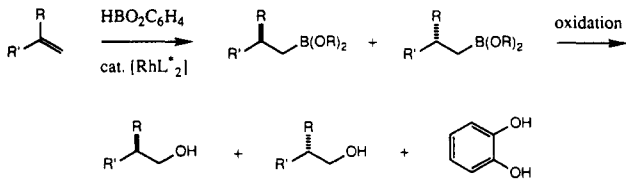
reagent-controlled diastereoselectivity



Methodology for reagent-controlled diastereoselectivity in hydroborations is limited by the following constraints: (i) large-scale reactions require prior syntheses of multigram quantities of air-sensitive chiral boranes; (ii) diastereoselection in hydroborations of alkenes other than *Z*-alkenes tends to be less than the level required for many asymmetric syntheses; (iii) the chiral hydroborating reagent is not easily regenerated from the reaction; and (iv) direct oxidation of the intermediate borane generates two equivalents of auxiliary (e.g. 3-pinanol, IpcOH) which can complicate purification of the product.

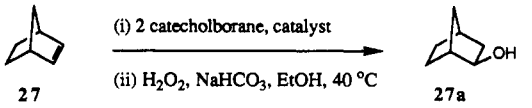
Asymmetric hydroborations of prochiral alkenes also can be effected using monochiral catalysts. This approach relegates the requisite diastereoselective steps to within a catalytic cycle, and the overall process is enantioselective. Asymmetric hydroborations of this kind are conceptually superior because (i) an achiral boron hydride is used; (the only optically active material required is a relatively small quantity of ligand for the catalyst) and (ii) the product is not contaminated with large quantities of substances formed from chiral auxiliaries, the byproduct from catecholborane hydroboration/oxidations is catechol, and this can be removed by simple extraction with aqueous base.

enantioselectivity



The enantioselective hydroborations of alkenes reported to date generally afford less induction than is required for contemporary asymmetric syntheses, but these preliminary studies are encouraging nevertheless. Representative hydroborations of norbornene are given in Table I;[21] *exo*-norborneol **27a** is the only product detected (NMR) in each case. Induction increases as the reaction temperature is decreased to −25 °C (entries 1–4) but, for this particular substrate, no marked improvement is observed on reducing the temperature from −25 °C to −40 °C. Entries 6, 4, and 7 demonstrate reducing the catalyst concentration below 2 mol % of rhodium atoms decreases the induction obtained. Catalysts derived from the ligands DIOP and BINAP

TABLE I. Enantioselective Hydroborations of Norbornene



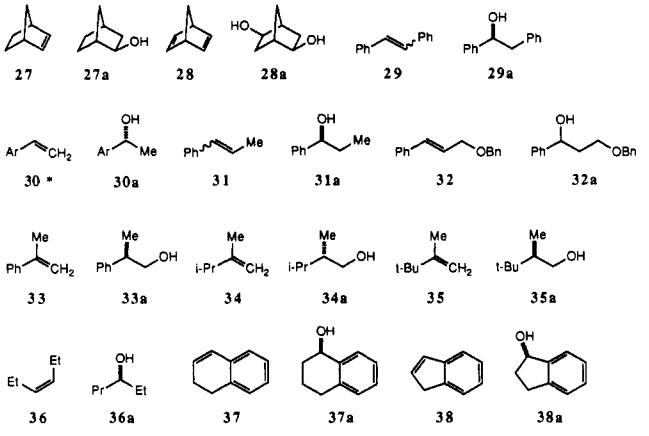
27 27a

entry	temp, °C	solvent	catalyst system	product, % ee[a] (config)
1	40	C_6H_6	2.5 mol % $[Rh(COD)Cl]_2$·2(*R,R*)-DIOP	22 (1*R*,2*R*)
2	5	C_6H_6	2.5 mol % $[Rh(COD)Cl]_2$·2(*R,R*)-DIOP	31 (1*R*,2*R*)
3	-5	THF	1.0 mol % $[Rh(COD)Cl]_2$·2(*R,R*)-DIOP	43 (1*R*,2*R*)
4	-25	THF	1.0 mol % $[Rh(COD)Cl]_2$·2(*R,R*)-DIOP	54 (1*R*,2*R*)
5	-40	THF	1.0 mol % $[Rh(COD)Cl]_2$·2(*R,R*)-DIOP	55 (1*R*,2*R*)
6	-25	THF	0.25 mol % $[Rh(COD)Cl]_2$·2(*R,R*)-DIOP	43[b] (1*R*,2*R*)
7	-25	THF	2.5 mol % $[Rh(COD)Cl]_2$·2(*R,R*)-DIOP	55[b] (1*R*,2*R*)
8	-25	THF	0.5 mol % $[Rh(COD)Cl]_2$·2(*R*)-BINAP	62 (1*R*,2*R*)
9	-25	THF	0.5 mol % $[Rh(COD)Cl]_2$·2(*S,S*)-CHIRAPHOS	15 (1*S*,2*S*)

[a] Determined by ^1H NMR analysis of the MPTA ester, unless otherwise indicated. [b] Determined via ^1H NMR analysis with $Eu(hfc)_3$ chiral shift reagent.

TABLE II. Enantioselective Hydroborations of Alkenes 27–38

entry	alkene	temp, °C	solvent	catalyst system	product, % ee (config)	ref
1	**28**	-25	THF	1.0 mol % $[Rh(COD)Cl]_2$·2(*R,R*)-DIOP	76 (1*S*,2*R*)	21
2	***Z*-29**	-25	THF	1.0 mol % $[Rh(COD)Cl]_2$·2(*R,R*)-DIOP	19 (*S*)	21
3	**30**	-78	DME	1.0 mol % $[Rh(COD)_2][BF_4]$·(*R*)-BINAP	96 (*R*)	35
4	**4-Cl-30**	-78	DME	1.0 mol % $[Rh(COD)_2][BF_4]$·(*R*)-BINAP	91 (*R*)	35
5	**4-MeO-30**	-78	DME/THF	1.0 mol % $[Rh(COD)_2][BF_4]$·(*R*)-BINAP	89 (*R*)	35
6	**2-MeO-30**	-30	THF	1.0 mol % $[Rh(COD)_2][BF_4]$·(*R*)-BINAP	82	35
7	***Z*-31**	-5	MePh	0.5 mol % $[Rh(COD)Cl]_2$·2(*S,S*)-DIOP	47 (*S*)	36
8	***E*-31**	-5	MePh	0.5 mol % $[Rh(COD)Cl]_2$·2(*S,S*)-DIOP	41 (*S*)	36
9	**32**	25	THF	1.0 mol % $[Rh(COD)Cl]_2$·2(*R,R*)-DIOP	16	18
10	**33**	-5	THF	1.0 mol % $[Rh(COD)Cl]_2$·2(*R,R*)-DIOP	27 (*R*)	21
11	**33**	-5	MePh	0.5 mol % $[Rh(COD)Cl]_2$·2(*S,S*)-CHIRAPHOS	16 (*S*)	36
12	**33**	-5	MePh	0.5 mol % $[Rh(COD)Cl]_2$·2(*S,S*)-BPPFA	7 (*R*)	36
13	**34**	-5	MePh	0.5 mol % $[Rh(COD)Cl]_2$·2(*S,S*)-DIOP	12 (*S*)	36
14	**35**	-5	THF	1.0 mol % $[Rh(COD)Cl]_2$·2(*R,R*)-DIOP	69 (*R*)	21
15	**36**	-5	MePh	0.5 mol % $[Rh(COD)Cl]_2$·2(*S,S*)-DIOP	10 (*S*)	36
16	**37**	-5	MePh	0.5 mol % $[Rh(COD)Cl]_2$·2(*S,S*)-DIOP	14 (*R*)	36
17	**38**	-30	MePh	0.5 mol % $[Rh(COD)Cl]_2$·2(*S,S*)-DIOP	74 (*R*)	36



* For derivatives of compound **30**:

Ar	compound 30
C_6H_5	30
4-ClC_6H_4	4-Cl-30
4-$MeOC_6H_4$	4-MeO-30
2-$MeOC_6H_4$	2-MeO-30

Figure 1. Substrates and products of enantioselective catalyzed hydroborations.

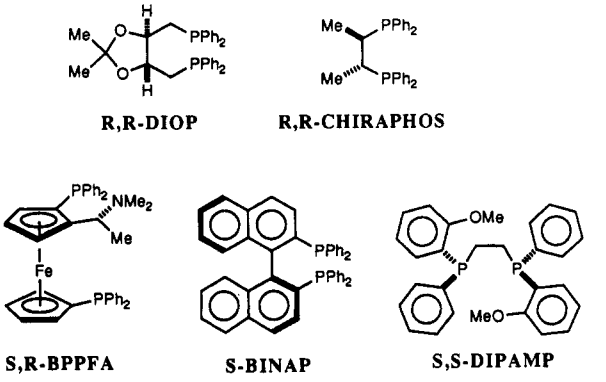


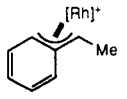
Figure 2. Chiral phosphine ligands used for catalyzed hydroborations of substrates **27–38**.

(Figure 2) tend to give good induction, while results with CHIRAPHOS are less encouraging (entry 9).

Table II summarizes enantioselective hydroborations of other alkenes (see also Figure 1).[21,35,36,37] Norbornadiene gives the corresponding chiral diol **28a** with relatively high optical purity (entry 1), but this result is deceptive since formation of meso diol effectively enhances the induction. Termination of the catalyzed hydroboration of (*Z*)-1,2-diphenylethene (***Z*-29**) before completion gives significant quantities of (*E*)-1,2-diphenylethene (***E*-29**); this probably reduces the optical yield of **29a** because reaction of ***E*-29** under the conditions shown in entry 2 is almost stereorandom.

Hydroborations of phenylethene derivatives (**30**) (entries 3–5, Table II) give the highest optical yields observed in catalyzed hydroborations. Enantioselectivities in these processes are not diminished by electron-releasing or electron-withdrawing aryl-substituents, but increased steric hindrance decreases the induction slightly (entry 6). The most remarkable feature of these

reactions, however, is that they proceed with high regioselectivity (>99:1 in some cases) in favor of the internal boronate ester.[64] This Markovnikov selectivity apparently is only observed for hydroborations of *aryl-substituted* alkenes mediated by *cationic* rhodium(+1) complexes: hydroboration of styrene mediated by a *neutral* catalyst, $RhCl(PPh_3)_3$, under the standard conditions was reported to give the secondary alcohol (**30a**) and 2-phenylethanol in a 10:90 ratio, and hydroboration of 1-octene under the same conditions affords 92:8 selectivity in favor of the primary alcohol. It has been suggested[35] that anomalous regioselectivities in hydroborations of aryl-substituted alkenes can be attributed to cationic η^3-benzylrhodium intermediates (c.f. **39**).

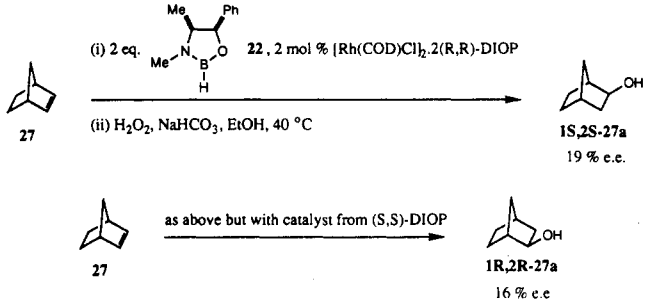


39

More recent work indicates phosphine-to-rhodium ratios are critical in hydroborations of styrene derivatives: higher ratios (i.e. more phosphine) favors formation of the secondary boronate ester even with neutral catalysts.[24,38]

Reagent-controlled diastereoselectivity is generally ineffective for asymmetric hydroborations of 1,1-disubstituted alkenes (e.g. 1.4% de for hydroboration of $^iPrMeC{=}CH_2$ with a reagent which is effective in many other cases).[39] Appreciable induction in enantioselective hydroborations of these substrates (Table II, entries 10–14, up to 69% ee) bodes well for the future of these reactions.

Another variable that might prove to be important in enantioselective hydroborations is the boron hydride reagent. Hydroboration of norbornene[37] and styrene derivatives[40] by the ephedrine derivative **22**,[41] gives induction *opposite to that observed when catecholborane with the same chiral phosphine ligand is used.* Catalysts based upon (*S,S*)-DIOP and (*R,R*)-DIOP give opposite enantioselectivities in the reaction of norbornene with oxazolidine **22**; consequently, the change in the sense of the induction observed for catecholborane and **22** is not due to the chirality in the heterocyclic ring. This reversal of induction is a consequence

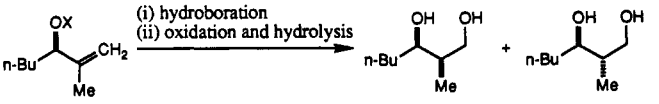


of the structure of the borane hydride, but chiral centers in the reagent have minimal stereochemical influence. Enantioselectivity in catalyzed hydroborations therefore could be very dependent on the nature of the boron hydride reagent.[37]

IV. Substrate-Controlled Diastereoselectivity

A fundamental issue in organic syntheses is control of relative stereochemistry. The value of catalyzed hydroborations in this respect was first illustrated for hydroborations of allylic alcohol derivatives, and this led to speculation concerning the stereoelectronic effects operative in these reactions. Later, these investigations were expanded to include allylic amines.

TABLE III. Hydroborations of Allylic Alcohol Derivatives 40



40 **syn** **anti**

entry	X	method	syn:anti	ref(s)
1	H	*catalyzed*[a]	69:31	22, 39, 40
2	H	*uncatalyzed*[b]	8:92	41
3	$COCH_3$	*catalyzed*	73:27	39, 40
4	$COCH_3$	*uncatalyzed*	12:88	41
5	CO^tBu	*catalyzed*	87:13	40
6	CO^tBu	*uncatalyzed*	6:94	40
7	$COCF_3$	*catalyzed*	88:12	39, 40
8	$COCF_3$	*uncatalyzed*	7:93	41
9	THP	*catalyzed*	89:11	40
10	THP	*uncatalyzed*	21:79	40
11	CPh_3	*catalyzed*	95:5	40
12	CPh_3	*uncatalyzed*	15:85	41
13	$^tBuMe_2Si$	*catalyzed*	96:4	22
14	$^tBuMe_2Si$	*uncatalyzed*	10:90	41
15	$^tBuPh_2Si$	*catalyzed*	96:4	22
16	$^tBuPh_2Si$	*uncatalyzed*	14:86	41
17	$CONMe_2$	*catalyzed*	71:29	39, 40

[a] Catecholborane, <2 mol % Rh catalyst, throughout. [b] 9-BBN, throughout.

A. Acyclic Allyl Alcohol Derivatives

Catalyzed hydroborations of the allylic alcohol derivatives **40** are "stereocomplementary" to conventional hydroborations of the same substrates;[22,42,43] all the rhodium-mediated processes shown in Table III give predominantly syn product whereas the corresponding uncatalyzed processes[44] are anti selective (Table III).

Catalyzed hydroboration of the allylic acetate (Table III, entry 3) is a useful reference point. Syn selectivity is increased in the catalyzed hydroborations by replacing the acetate with a bigger group (e.g. pivalate, entry 5), or with a more electron-withdrawing group (e.g. trifluoroacetate, entry 7), indicating both steric *and electronic*[42] features are important. Replacement of acetate with *N,N*-dimethylcarbamate, however, has little effect on the stereoselectivity implying transient coordination is probably not involved in these reactions (entry 17). Indeed, only very strongly coordinating groups have been reported to influence the stereochemical outcome of rhodium-mediated hydroborations in this way[22] (vide infra).

B. Stereoelectronic Effects in Rhodium-Catalyzed Hydroborations

A model has been proposed to account for substrate-controlled diastereoselectivities in rhodium-catalyzed hydroborations of acyclic allylic alcohol derivatives and similar substrates.[43,45] It assumes the diastereofacial selectivity of coordination of rhodium determines the stereochemical outcome of these reactions, either in a kinetic sense or by influencing equilibrating diastereomeric alkene complexes. There is no direct

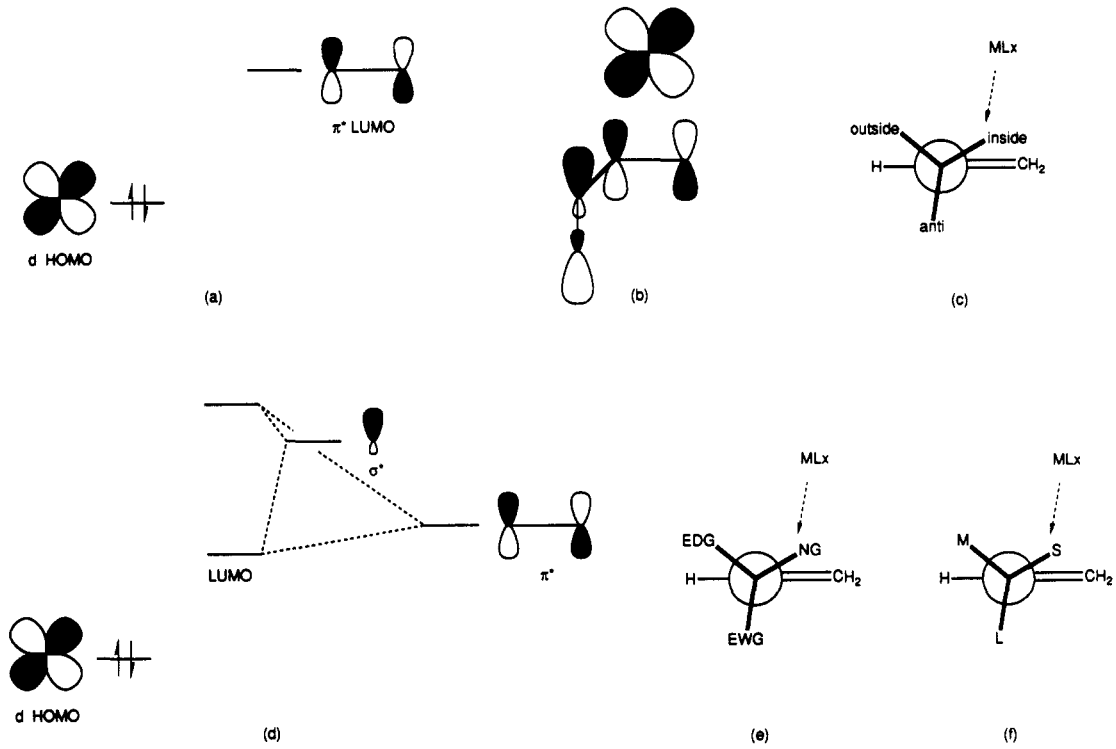


Figure 3. Parts are designated as follows: (a) primary interaction in coordination of a chiral allylic alkene to a transition-metal complex; (b) orbitals involved in the primary and secondary interactions; (c) approximate orientation required to achieve overlap; (d) secondary interaction in coordination of a chiral allylic alkene to a transition-metal complex (it lowers the LUMO relative to the primary interaction alone); (e) preferential orientation based on electronic demands of the substituents; (f) preferential orientation in metal-catalyzed hydroborations based on steric demands of the substituents.

evidence for coordination of the alkene being the determinant feature in these reactions. Nevertheless, if one accepts this assumption, the argument presented below can be used to explain the sense of substrate-controlled diastereoselectivity in catalyzed hydroborations of acyclic α-chiral alkenes.

Briefly, the postulate states there are two components to diastereofacial bias, electronic and steric. Electronic influences can be assessed by considering the frontier orbital interaction for π-complexation of a transition metal: the filled d orbital of the metal (HOMO) and the π*-orbital of the alkene (LUMO, i.e. Dewar–Chatt bonding, Figure 3a).[46] Stereoselectivity will arise if there is a reactive conformation of the alkene which affords net stabilization of the bond forming between these two components. Mixing the σ*-orbital associated with the bond at the chiral center which is anti to the approaching metal, with the π*-orbital of the alkene (Figure 3, parts b and c) facilitates this by closing the HOMO–LUMO energy gap (Figure 3d). The group with the lowest energy σ*-orbital will occupy this crucial anti position, i.e. the best electron-withdrawing group (EWG) (Figure 3e). Consequently, when predicting the sense of diastereofacial selectivity, one should place the best σ-acceptor in the anti position. The smallest substituent on the chiral center (e.g. some small, electronically neutral group, NG) will occupy the "inside crowded"[47] position in the reactive conformation (the sterically most congested site due to the approach of the metal, vide infra).

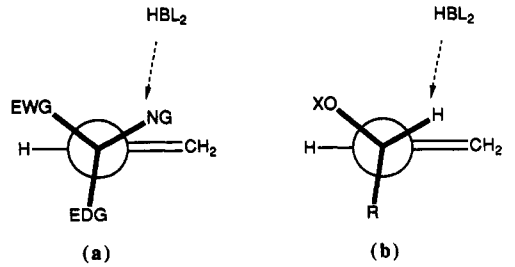
On the basis of steric effects alone, one would anticipate the largest group (L) would tend to orientate away from (or anti to, Figure 3f) the approaching reagent, with the next largest substituent (M) preferentially in the "outside" position[47] which is less encumbered than the "inside crowded" site.

When the electronic and steric effects are working in opposition, the models described above predict less than optimum selectivity; however, they are of little value beyond this unless the relative magnitude of the steric and electronic contributions is known. Conversely, electronic and steric effects reinforce each other when the best σ-acceptor is also the largest substituent, and good diastereofacial selectivity should result. Thus, on the basis of these arguments: *diastereoselection in catalyzed hydroborations of allylic alcohol derivatives will be optimum if the protected alcohol is a good σ-acceptor, and is large, relative to the other substituents on the asymmetric center.*[43]

Review of Table III shows the hypothesis presented above is consistent with the observed selectivities. Taking the acetate in entry 3 as a basis for comparison of the catalyzed hydroborations reveals syn selectivity is directly related to electronic effects (c.f. the increase observed for the trifluoroacetate, entry 7) and to steric effects (c.f. the increase for the pivalate, entry 5).

These conclusions are fundamentally different from those obtained by using similar reasoning for conventional hydroborations.[48] For these reactions, it is the electron donating group which orients anti to the approaching borane in the reactive conformation, giving the opposite diastereoselectivity (Figure 4, Table III).

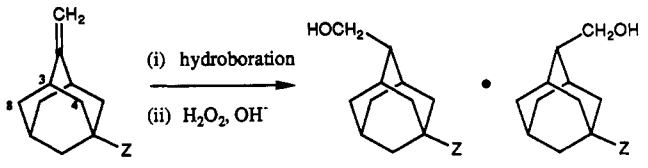
Model reactions to test the hypothesis for electronic effects in catalyzed hydroborations outlined above should eliminate steric effects as far as possible. Hydroborations of the fluorinated substrate **45** have been used,[43] the catalyzed and uncatalyzed reactions are stereocomplementary, and the sense of these selectiv-



(a) (b)

Figure 4. Reactive conformations for uncatalyzed hydroborations: (a) based on electronic demands of the substituents; and (b) in hydroboration of an allylic alcohol derivative.

TABLE IV. Catalyzed and Uncatalyzed Hydroborations of Alkenes 47

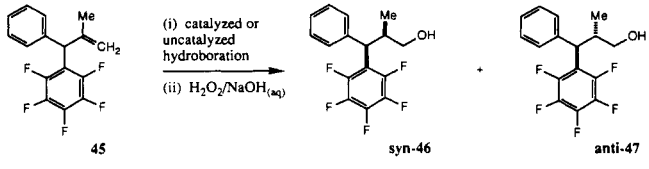


47 *anti* *syn*

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

[a] Substrate:catecholborane = 1.0:1.5, 2 mol % $[Rh(COD)Cl]_2$, 4 mol % PPh_3, THF, −78 to 25 °C, 12 h. [b] Equimolar amounts of substrate and BH_3·THF, THF, −78 to 25 °C, 12 h. [c] Substrate:9-BBN = 1.0:1.5, THF, −78 to 25 °C, 36 h. [d] Substrate:catecholborane = 1.0:8.0, THF, 70 °C, 2 h.

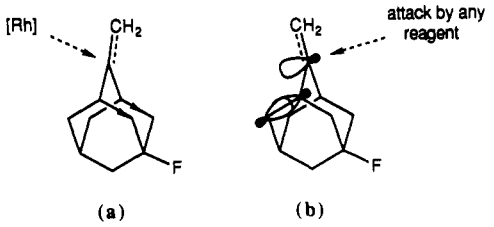
ities is in accord with the frontier orbital arguments outlined above.



45 syn-46 anti-47

	syn:anti
2 eq. catecholborane, 1 mol % $[Rh(COD)Cl]_2$, 4 mol % PPh_3, 25 °C, 48 h	2.5:1.0
2 eq. catecholborane, 2 mol % $[RhCl(PPh_3)_3]$, 25 °C, 48 h	1.9:1.0
2 eq. 9-BBN, - 25 °C, 72 h	1.0:1.5

Steric effects cannot be completely discounted, however, in hydroborations of alkene **45**, because pentafluorophenyl is larger than phenyl; a more rigorous probe for electronic effects is outlined in Table IV.[49] These data show small but measurable preferences for catalyzed hydroborations of methyleneadamantanes **47** on the alkene face opposite to electron-withdrawing 5-substituents (giving excess syn product, entries 1 and 5), and on the same face as an electron-releasing substituent ($SiMe_3$, entry 7). The 5-substituents of these adamantane derivatives are unlikely to have any steric influence on reactions of the alkene, but hyperconjugation lowers (X = F or Ph) or elevates (X = $SiMe_3$) the energy of the $C_{3,4}$ bonds relative to the analogous $C_{3,8}$ linkages on the opposite π-face, causing *electronic* perturbations. Consequently, any facial selectivities observed in the reactions of these substrates probably



(a) (b)

Figure 5. Models for rhodium-catalyzed hydroborations of adamantane derivatives: (a) based on secondary orbital effects involving $d\pi$–$p\pi$ interactions; and (b) from extrapolation of the Cieplak postulate.

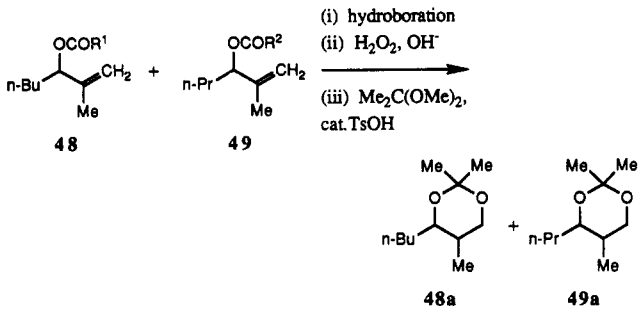
reflect electronic effects, provided there are no unusual solvation factors. If one accepts that there is an analogy between the conformation shown in Figure 3e and interactions of rhodium complexes with the rigid alkenes **47** (e.g. Figure 5a), then these results are *in perfect accord with the frontier orbital postulate outlined above.*

Conventional hydroborations of alkenes **47** give the opposite isomer preferentially, an observation which is both consistent with frontier orbital arguments and the "Cieplak postulate" (i.e. stabilization of the incipient σ^* via overlap with the highest energy σ-bond(s), in this case those of the C^3–C^4 or C^3–C^8 linkages; Figure 5b).[50,51] Indeed, nearly all the reported reactions of 5-substituted adamantane derivatives proceed with this stereochemical bias.[52-56] Opposite stereoselectivity in the catalyzed hydroborations of these systems are, apparently at least, contrary to the Cieplak postulate. Many of the experiments shown in Table IV (run in THF) were repeated with use of toluene as a solvent, and no appreciable change in selectivity was observed.[49] Others have suggested solvation may be important for model compounds used to test the Cieplak hypothesis,[57] but solvent apparently is not a crucial factor in these experiments.

Another consequence of the ideas depicted in Figure 5 is that alkenes bearing strongly electron withdrawing groups at an α-asymmetric center should undergo *faster* catalyzed hydroborations than similar substrates without such substituents, because the HOMO–LUMO gap is less in the former case. This idea was explored in the competition experiments depicted in Table V.[49] Near equimolar mixtures of the similar substrates were hydroborated by using 0.05 equiv of catecholborane in the presence of rhodium(+1) complexes, oxidized, and treated with 2,2-dimethoxypropane; ratios of the acetonide products were measured by GC. This protocol establishes values for *minimum* rate ratios due to approximations inherent in experiments of this type.

Entry 1 of Table V proves substitution of *n*-butyl with *n*-propyl has no significant effect on the rate of hydroboration, hence rate differences in subsequent experiments can be attributed to the substituent "X". 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; the trifluoroacetate reacts approximately four times *slower* than the acetate. This is not surprising; the proposed reactive conformation for uncatalyzed hydroborations of these substrates (with the electron-donating group in the anti position, Figure 4)[44,48] does not

TABLE V. Relative Rates of Hydroborations of Allylic Alcohol Derivatives 35 and 36



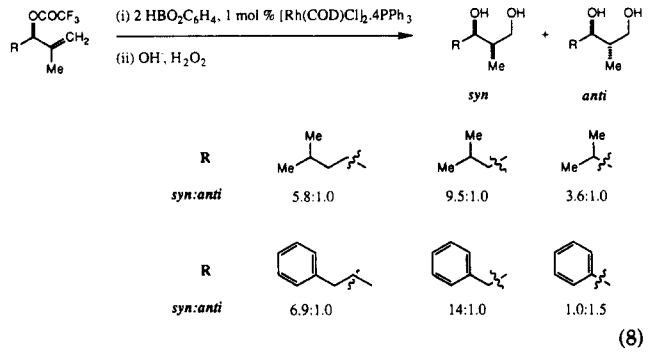
entry	R^1	R^2	conditions	48a:49a[a]
1	Me	Me	*catalyzed*[b]	1.0:1.2
2	Me	CF_3	*catalyzed*	1:160
3	CF_3	Me	*catalyzed*	210:1
4	CF_3	Me	*uncatalyzed*[c]	1.0:4.9
5	Me	^{t}Bu	*catalyzed*	2.7:1.0
6	^{t}Bu	Me	*catalyzed*	1.0:3.5

[a] Products formed as diastereomeric mixtures but the ratios quoted are **48a**(syn + anti):**49a**(syn + anti); determined via capillary GC and corrected for the detectors response to each compound. [b] Substrate:catecholborane:$RhCl(PPh_3)_3$ = 1.00:0.05:0.005. Reaction conditions: 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-methylsulfonic acid at 25 °C for 2 h. [c] Hydroboration performed by using 0.05 equiv of 9-BBN and processed as described in note *b*.

facilitate mixing of COCOR orbitals with the π-system, hence one would not anticipate rate acceleration for the trifluoroacetate; on the contrary, *retardation* occurs due to greater inductive deactivation of the alkene toward electrophilic attack. Finally, competition between acetate- and pivalate-protected allylic alcohol derivatives (entries 5 and 6) demonstrate increased steric hindrance can retard the rate of catalyzed hydroborations, but this effect is much smaller than the influence of electronic perturbations.

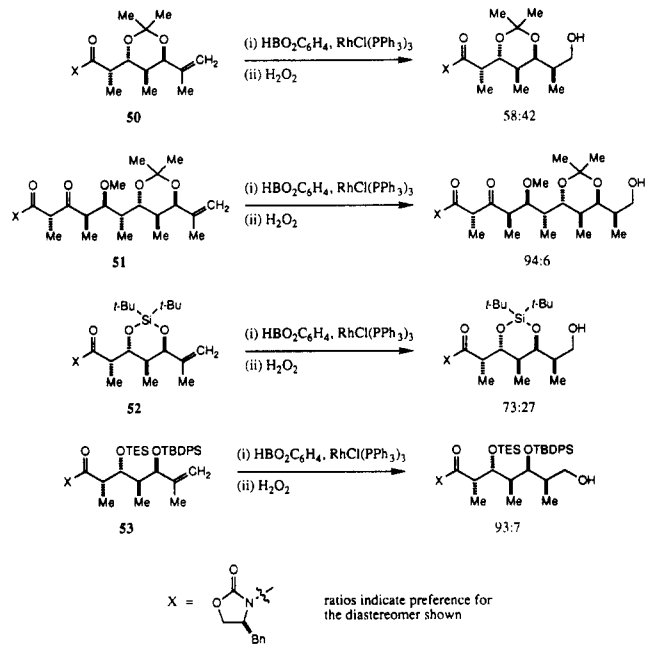
None of the model experiments described above prove the frontier orbital postulate for electronic effects in catalyzed hydroborations, and one might be skeptical in view of the mechanistic uncertainties involved. Nevertheless, they provide circumstantial evidence which is quite compelling. Moreover, no other explanation has been offered to the stereocomplentarity of catalyzed and uncatalyzed hydroborations, and we are unable to suggest an alternative that is consistent with the data summarized above.

Finally, some aspects of substrate-controlled diastereoselectivity in catalyzed hydroborations have yet to be explained satisfactorily. For instance, eq 8 shows a set of reactions designed to probe the steric influences of the "R" functionality in these reactions. Surprisingly, stereoselectivities do not steadily increase or decrease as the large substituent in the aliphatic chain is moved closer to the chiral center; instead maximum induction is observed when it is one methylene group removed from the asymmetric center.[58] Aromatic stacking conceivably could account for the results with phenyl-substituted substrates, but not for the behavior of the series of compounds with completely *aliphatic* R substituents. Consequently, substituent *shape* seems to be more important than absolute size when assessing diastereoselectivity in these reactions, but more detailed



(8)

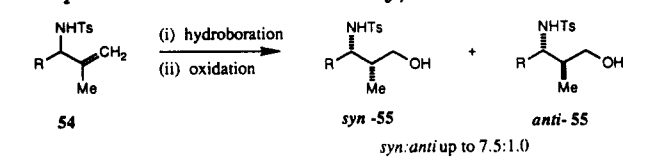
explanations of the origins of these effects remain to be formulated. The implications of this conclusion may be particularly important in complex organic syntheses, as illustrated by the extraordinary variance of substrate-controlled diastereoselectivity for catalyzed hydroborations of the stereochemically complex substrates **50–53**.[59] The "eastern sections" of alkenes **50** and **51** are identical yet the diastereoselectivity observed in hydroborations of these substrates differs very significantly.



The hypotheses presented in the first part of this section have predictive value; however the results summarized above indicate they are clearly more reliable for small molecules than for advanced intermediates in complex syntheses.

C. Acyclic Allylamine Derivatives.

Optically active allylamine derivatives **54** have been prepared from amino acids to study their behavior in catalyzed and uncatalyzed hydroborations. The results indicate the catalyzed hydroborations tend to be syn selective, whereas the uncatalyzed hydroborations with 9-BBN are nonselective or anti selective.[58,60] These findings are consistent with the hypothesis outlined in the previous section. Usually, the crude reaction



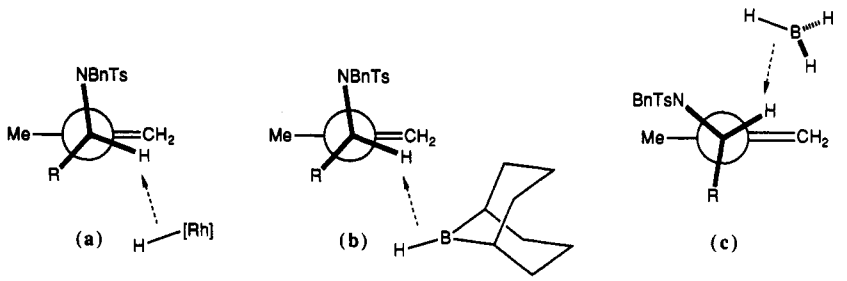
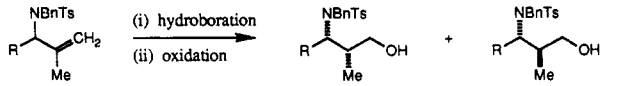


Figure 6. Reactive conformations in hydroboration of allylic *N*-(tosylbenzyl)amine derivatives: (a) under catalytic conditions; (b) with 9-BBN; and (c) with BH_3·THF.

mixtures could be recrystallized to give chemically and optically pure samples of the syn diastereomer; nevertheless, it would be advantageous to obtain higher diastereoselectivities in these reactions.

Derivatives **56**, with *N*-benzyl substituents, were prepared to enhance stereoselection in catalyzed hydroborations of allylamine derivatives (Table VI). The reasoning behind this modification was that the NBnTs group, being larger than NHTs, has a greater preference to orient away from the approaching metal in the reactive conformation (cf. Figure 3f), thus increasing syn selectivity. In fact, catalyzed hydroborations of these substrates do give higher syn selectivities than in the corresponding series of allylamine derivatives without *N*-benzyl substituents.[60] Anti products are preferentially obtained when BH_3·THF is used in these hydroborations (entries 3, 6, 9, and 11), just as one might expect on the basis of parallels with the allylic alcohol series. Uncatalyzed hydroborations of alkenes **56** with 9-BBN were syn selective, however, this surprising result may be attributed to severe steric interactions between the 9-BBN and NBnTs entities, forcing them to orient away from each other, whereas with BH_3·THF the corresponding interactions are less significant and the expected reactive conformation dominates (Figure 6, see Figure 4 for comparison).

TABLE VI. Hydroborations of *N*-(Benzyltosyl) Substrates 56



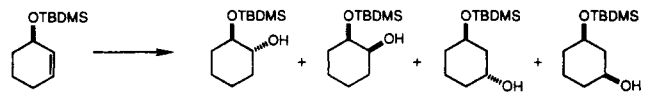
56 *syn*-57 *anti*-57

entry	R	method[a]	syn:anti
1	$PhCH_2$	$C_6H_4O_2BH$/cat. [Rh][b]	95:5
2	$PhCH_2$	9-BBN[c]	93:7
3	$PhCH_2$	BH_3[d]	6:94
4	Bu	$C_6H_4O_2BH$/cat. [Rh]	91:9
5	Bu	9-BBN	87:13
6	Bu	BH_3	5:95
7	$^iPrCH_2$	$C_6H_4O_2BH$/cat. [Rh]	86:14
8	$^iPrCH_2$	9-BBN	96:4
9	$^iPrCH_2$	BH_3	5:95
10	$^tBuO_2CCH_2$	9-BBN[e]	84:16
11	$^tBuO_2CCH_2$	BH_3[e]	2:98

[a] Oxidation with $NaOH/H_2O_2$ unless otherwise indicated. [b] Catalyzed hydroborations were performed with use of THF solutions of 2 mol % of $[Rh(COD)Cl]_2$·$4PPh_3$, 3 equiv of catecholborane at 25 °C for 48 h. [c] 9-BBN hydroborations were performed with use of THF solutions of 3 equiv of 9-BBN at −78 to 25 °C then at 25 °C for 24 h. [d] BH_3 hydroborations were performed with use of THF solutions of 3 equiv of BH_3·THF at −78 to 25 °C then at 0 °C for 24 h. [e] Oxidation with $NaOAc/H_2O_2$; use of more basic conditions tends to decompose the product.

V. Regioselectivity[64]

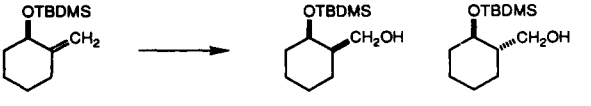
Catalyzed and uncatalyzed hydroboration/oxidations of the cyclohexenol **58** give different product distributions which vary slightly with the nature of the oxygen protecting group.[22] Preferential formation of 1,3-diols



58 *anti*-59 *syn*-59 *anti*-60 *syn*-60

conditions	*anti*-59	*syn*-59	*anti*-60	*syn*-60
3 eq. 9-BBN, THF, 25 °C	74	0	13	13
3 eq. $HBO_2C_6H_4$, 3 mol % $RhCl(PPh_3)_3$, 25 °C	2	1	86	11

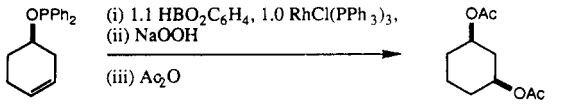
in the catalyzed hydroborations is probably a consequence of the steric demands of the metal. Selectivity in favor of the anti product in these catalyzed hydroborations is unlikely to be due to steric effects because the OSi^tBuMe_2 (OTBDMS) substituent occupies a pseudoequatorial position with respect to the cyclohexene ring. Anti selectivity could be due to relatively fast reaction of a small equilibrium concentration of the conformer with a pseudoaxial silyl ether substituent, with the metal approaching opposite this group (c.f. section III.B). Similarly syn selectivity in the hydroboration of the exocyclic alkene **61** can be explained in terms of a combination of steric and electronic effects.



61 *syn*-62 *anti*-62

conditions	*syn*-62	*anti*-62
3 eq. 9-BBN, THF, 25 °C	39	61
3 eq. $HBO_2C_6H_4$, 3 mol % $RhCl(PPh_3)_3$, 25 °C	96	4

Hydroborations of the cyclic alkene **63**, gives almost exclusively *syn* products presumably due to coordination of rhodium to the phosphorus site.[22] Such reactions have little or no value for organic syntheses because *stoichiometric* quantities of rhodium complex are required to obtain good yields.[65]

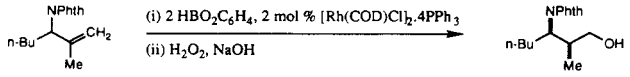


63 85 %
syn-selectivity >50:1

VI. Chemoselectivity

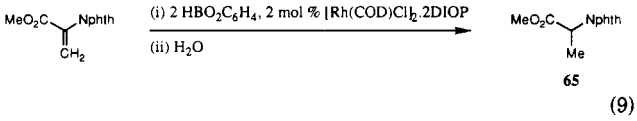
This review began with an example in which rhodium complexes facilitate hydroborations of alkene functionality in preference to a ketone group, it ends with more examples of this phenomenon.

Catalyzed hydroboration/oxidations of the phthalyl-protected allylic amines (e.g. **64**) give up to 44% isolated yields of the corresponding alcohols, whereas the phthalyl group is reduced in conventional hydroborations of the same substrates with 9-BBN.

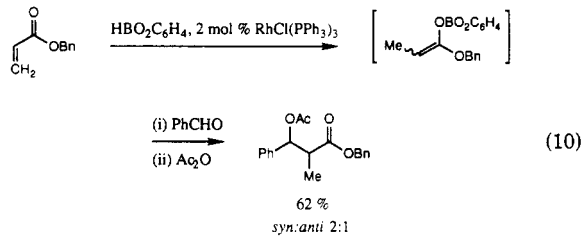


64 44 %
syn:*anti* >95:5

Rhodium(+1) complexes also promote additions of catecholborane to some α,β-unsaturated carbonyl compounds but, just as in similar uncatalyzed reactions, boron *enolates* are formed.[61] Aqueous workup of these reactions gives the corresponding protonated products (eq 9),[62] but the reactions can also be quenched using other electrophiles (eq 10).[63]



65 (9)



62 % (10)
syn:*anti* 2:1

Uncatalyzed hydroborations of α,β-unsaturated carbonyl compounds apparently proceed through a [$4\pi + 2\sigma$] transition structure producing *Z* enolates selectively; subsequent aldol reactions of these enolates are highly diastereoselective in the sense that one would predict from reactions of *Z* boron enolates via chair-like transition states.[61] The corresponding catalyzed hydroboration/aldol sequence gives far less diastereoselectivity;[63] perhaps via conjugate addition of Rh–H (not B–H) in a transformation that does not involve a [$4\pi + 2\sigma$] interaction.

VII. Conclusion

Research outlined in this review demonstrates methodology for delivering B–H bonds to alkenes via a process which is mechanistically distinct from concerted additions of boranes; however, details of reaction pathways for the metal-mediated processes remain to be established. Issues of chemoselectivity, regioselectivity, and relative stereoselectivity can be addressed by using rhodium-catalyzed hydroborations, and there are reasons to believe practical methods for *enantioselective* additions may be developed. Most of the reactions described in this review are rhodium-mediated, but other catalysts have been identified and more still could be discovered.[65]

All the indications are that catalyzed hydroborations could become a standard procedure in synthetic organic chemistry.

Acknowledgments. We wish to thank Wilfred A. van der Donk (Rice), Dr. Todd Marder (University of Waterloo, Canada), and Dr. Tom Baker (Du Pont) for helpful discussions. Financial support was provided by The Robert A. Welch Foundation and the National Science Foundation.

Note Added in Proof. The deuterium labeling experiments depicted in eqs 5 and 6 of section II.A were performed by using commercial (i.e. "aged") Wilkinson's catalyst. The results originally reported for these two transformations (ref 23) can be reproduced by using catalyst prepared according to the procedure given in *Inorganic Syntheses* (Vol. X, p 67). Intentional exposure of this catalyst to oxygen dramatically alters the styrene hydroboration regiochemistry and deuterium regiochemistry, as well as deuterium incorporation in 1-decene. We thank Prof. D. A. Evans (Harvard) for pointing this out.

References

(1) Mannig, D.; Noth, H. *Angew. Chem., Int. Ed. Eng.* **1985**, *24*, 878.
(2) Brown, H. C. In *Hydroboration*; Wiley-Interscience: New York, 1962.
(3) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. In *Organic Syntheses via Boranes*; Wiley-Interscience: New York, 1975.
(4) Pelter, A.; Smith, K.; Brown, H. C. In *Borane Reagents*; Academic Press: New York, 1988.
(5) Wilczynski, R.; Sneddon, L. G. *J. Am. Chem. Soc.* **1980**, *102*, 2857.
(6) Wilczynski, R.; Sneddon, L. G. *Inorg. Chem.* **1981**, *20*, 3955.
(7) Wilczynski, R.; Sneddon, L. G. *Inorg. Chem.* **1982**, *21*, 506.
(8) Davan, T.; Corcoran, E. W.; Sneddon, L. G. *Organometallics* **1983**, *2*, 1693.
(9) Mirabelli, M. G. L. *Organometallics* **1986**, *5*, 1510.
(10) Hewes, J. D.; Kreimendahl, C. W.; Marder, T. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 5757.
(11) Mirabelli, M. G. L.; Sneddon, L. G. *J. Am. Chem. Soc.* **1988**, *110*, 449.
(12) Lynch, A. T.; Sneddon, L. G. *J. Am. Chem. Soc.* **1987**, *109*, 5867.
(13) Lynch, A. T.; Sneddon, L. G. *J. Am. Chem. Soc.* **1989**, *111*, 6201.
(14) Knorr, J. R.; Merola, J. S. *Organometallics* **1990**, *9*, 3008.
(15) 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.
(16) Kono, H.; Ito, K. *Chem. Lett.* **1975**, 1095.
(17) Westcott, S. A.; Taylor, N. J.; Marder, T. B.; Baker, R. T.; Jones, N. J. *J. Chem. Soc., Chem. Commun.* **1991**, 304.
(18) Burgess, K.; Ohlmeyer, M. J.; van der Donk, W. A. Unpublished results.
(19) Marder, T. Personal communications.
(20) Evans, D. A.; Hoveyda, A. H. *J. Org. Chem.* **1990**, *55*, 5190.
(21) Burgess, K.; Ohlmeyer, M. J. *J. Org. Chem.* **1988**, *53*, 5178.
(22) Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 6917.
(23) Evans, D. A.; Fu, G. C. *J. Org. Chem.* **1990**, *55*, 2280.
(24) Burgess, K.; van der Donk, W. A.; Kook, A. M. *J. Org. Chem.* **1991**, *56*, 2949.
(25) Matsuda, I.; Kato, T.; Sato, S.; Izumi, Y. *Tetrahedron Lett.* **1986**, *27*, 5747.
(26) Stille, J. K.; Becker, Y. *J. Org. Chem.* **1980**, *45*, 2139.
(27) Satoh, M.; Nomoto, Y.; Miyaura, N.; Suzuki, A. *Tetrahedron Lett.* **1989**, *30*, 3789.
(28) Isagawa, K.; Sano, H.; Hattori, M.; Otsuji, Y. *Chem. Lett.* **1979**, 1069.

(29) Lee, H. S.; Isagawa, K.; Otsuji, Y. *Chem. Lett.* **1984**, 363.
(30) Lee, H. S.; Isagawa, K.; Toyoda, H.; Otsuji, Y. *Chem. Lett.* **1984**, 673.
(31) Lucas, C. R. *Inorg. Synth.* **1977**, *17*, 91.
(32) Isagawa, K.; Tatsumi, K.; Kosugi, H.; Otsuji, Y. *Chem. Lett.* **1977**, 1017.
(33) Brown, H. C.; Jadhav, P. K. Asymmetric Synthesis. In *Asymmetric Hydroboration*; Academic Press: New York, 1983.
(34) Brown, H. C.; Singaram, B. *Acc. Chem. Res.* **1988**, *21*, 287.
(35) Hayashi, T.; Matsumoto, Y.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3426.
(36) Sato, M.; Miraura, N.; Suzuki, A. *Tetrahedron Lett.* **1990**, *31*, 231.
(37) Burgess, K.; van der Donk, W. A.; Ohlmeyer, M. J. *Tetrahedron Asymmetry* **1991**, *2*, in press.
(38) Zhang, J.; Lou, B.; Guo, G.; Dai, L. *J. Org. Chem.* **1991**, *56*, 1670.
(39) Masamune, S.; Kim, B. M.; Pedersen, J. S.; Sato, T.; Veenstra, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 4549.
(40) Brown, J. M.; Lloyd-Jones, G. C. *Tetrahedron Asymmetry* **1990**, *1*, 869.
(41) Joshi, N. N.; Srebnik, M.; Brown, H. C. *Tetrahedron Lett.* **1989**, *30*, 5551.
(42) Burgess, K.; Ohlmeyer, M. J. *Tetrahedron Lett.* **1989**, *30*, 395.
(43) Burgess, K.; Cassidy, J.; Ohlmeyer, M. J. *J. Org. Chem.* **1991**, *56*, 1020.
(44) Still, W. C.; Barrish, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 2487.
(45) Burgess, K.; Ohlmeyer, M. J. *Tetrahedron Lett.* **1989**, *30*, 5861.
(46) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.
(47) Houk, K. N.; Paddon-Row, M. N.; Rondan, N. G.; Wu, Y.; Brown, F. K.; Spellmeyer, D. C.; Metz, J. T.; Li, Y.; Loncharich, R. J. *Science* **1986**, *231*, 1108.
(48) Houk, K. N.; Rondan, N. G.; Wu, Y.; Metz, J. T.; Paddon-Row, M. N. *Tetrahedron* **1984**, *40*, 2257.
(49) Burgess, K.; van der Donk, W. A.; Jarstfer, M. B.; Ohlmeyer, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 6139.
(50) Cieplak, A. S. *J. Am. Chem. Soc.* **1981**, *103*, 4540.
(51) Cieplak, A. S.; Tait, B. D.; Johnson, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 8447.
(52) Cheung, C. K.; Tseng, L. T.; Lin, M.; Srivastava, S.; le Noble, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 1598.
(53) Srivastava, S.; le Noble, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 5874.
(54) Lin, M.; Silver, J. E.; le Noble, W. J. *J. Org. Chem.* **1988**, *53*, 5155.
(55) Xie, M.; le Noble, W. J. *J. Org. Chem.* **1989**, *54*, 3836.
(56) Xie, M.; le Noble, W. J. *J. Org. Chem.* **1989**, *54*, 3839.
(57) Durkin, K. A.; Liotta, D. *J. Am. Chem. Soc.* **1990**, *112*, 8162.
(58) Burgess, K.; Ohlmeyer, M. J. *Tetrahedron Lett.* **1989**, *30*, 5857.
(59) Evans, D. A.; Sheppard, G. S. *J. Org. Chem.* **1990**, *55*, 5192.
(60) Burgess, K.; Ohlmeyer, M. J. *J. Org. Chem.* **1991**, *56*, 1027.
(61) Boldrini, G. P.; Mancini, F.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Chem. Soc., Chem. Commun.* **1990**, 1680.
(62) Burgess, K.; Ohlmeyer, M. J. Unpublished results.
(63) Evans, D. A.; Fu, G. C. *J. Org. Chem.* **1990**, *55*, 5678.
(64) Very recently, asymmetric double hydroboration of 1,3-dienes catalyzed by rhodium(+1) complexes has been reported to give anti-1,3 products in up to 67% ee (Matsumoto, Y.; Hayashi, T. *Tetrahedron Lett.* **1991**, *32*, 3387).
(65) Amide-directed, iridium-catalyzed hydroborations using 5 mol % of catalyst have been reported very recently. (Evans, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **1991**, *113*, 4042).