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Rh-Catalyzed Enantioselective Diboration of Simple Alkenes: Reaction Development and Substrate Scope

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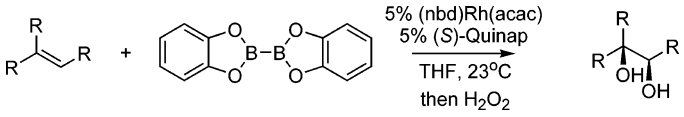
Received August 5, 2005



The rhodium-catalyzed reaction between bis(catecholato)diboron and simple alkenes results in the syn addition of the diboron across the alkene. The resulting 1,2-bis(boronate) is subsequently oxidized to provide the 1,2-diol. In the presence of enantiomerically enriched Quinap ligand, high enantioselection in the diboration can be achieved. The reaction is highly selective for trans- and trisubstituted alkenes and can be selective for some monosubstituted alkenes as well. The development of this reaction is described as is the substrate scope and experiments that are informative about the reaction mechanism and competing pathways.

Introduction

Stereospecific manipulation of carbon−boron bonds is sufficiently well developed that a large number of derivatives may be targeted through stereospecific replacement of the boron atom.[1] Amination,[2] oxidation,[3] catalytic[4] and stoichiometric cross-coupling,[5] and carbenoid insertions[6] all serve to create useful organic assemblies from common organoboron precursors. Because of this remarkable breadth, reactions that enable the synthesis of stereodefined carbon−boron bonds have significant value, and this is evidenced by the central role that hydroboration plays in contemporary organic synthesis.[7] While stereoselective insertion processes[8] also serve to create chiral organoboron compounds, there are few other methods for accessing these motifs in a selective fashion.

The catalytic reaction of alkenes with diboron compounds offers one route to organoboron reagents in a conceptually straightforward fashion.[9] This transformation furnishes two carbon−boron bonds, both of which might be derivatized in a useful fashion. Along these lines, it has been reported that alkene diboration may be accomplished with the assistance of rhodium,[10] platinum,[11] gold,[12] and silver[13] complexes. Each of these complexes is thought to catalyze diboration through a

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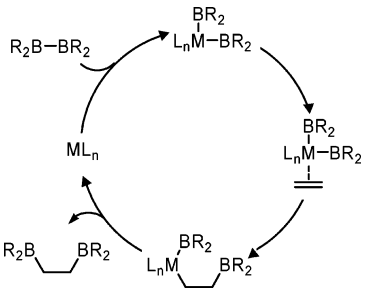
10.1021/jo051651m CCC: $30.25
Published on Web 10/20/2005

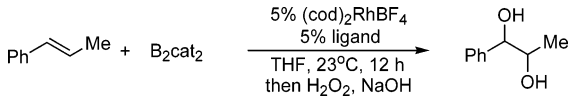
SCHEME 1. General Mechanism for Transition-Metal-Catalyzed Reaction by Alkenes and Diboron Compounds



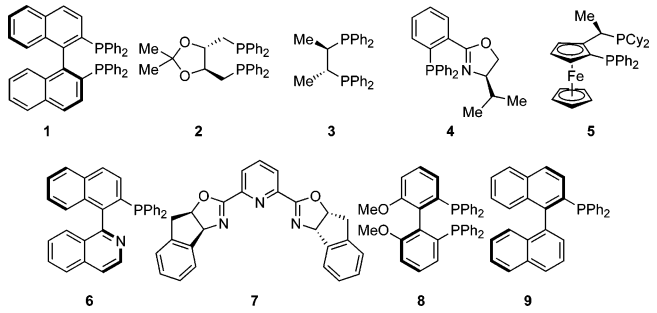
catalytic cycle that involves oxidative addition of the diboron reagent to the metal,[14] insertion of the alkene,[15] and then reductive elimination of the organodiboron product (Scheme 1).[16,17] Significant reaction side products are often observed that appear to arise from β-hydrogen elimination of the intermediate organometallic complex.[18]

In an effort to develop an asymmetric variant of the alkene diboration process, we initiated studies with chiral transition-metal complexes.[19] On the basis of the catalytic cycle described above, exploratory experiments were restricted to those involving bidentate chiral ligands in combination with rhodium complexes since it was expected that bidentate ligands would render the analogous four-coordinate d^8 platinum diboryl intermediate inert to olefin coordination and insertion reactions.[20] These initial experiments revealed that when chiral rhodium complexes derived from Quinap are used, the reaction exhibits remarkable enantioselection and good yields for a number of prochiral alkene substrates and that with this particular ligand structure the diboration process operates relatively free from competitive side reactions. While the diboron adduct may be conveniently oxidized to the 1,2-diol, selective tandem reactions are also possible and include tandem cross-coupling/oxidation[21] and homologation/oxidation.[22] In this manuscript we provide the full details of the reaction development, document the substrate scope, and provide a framework to forecast stereoinduction in these reactions.

TABLE 1. Survey of Chiral Ligands in the Rh-Catalyzed Alkene Diboration Reaction



entry	ligand	% yield	syn:anti	% ee syn (anti)
1	Binap (**1**)	25	1.5:1	38 (84)
2	DIOP (**2**)	37	4.5:1	5 (55)
3	Chiraphos (**3**)	<5		
4	*i*Pr-PHOX (**4**)	10	6.6:1	5
5	Josiphos (**5**)	<5		
6	Quinap (**6**)	24	35:1	86
7	Indane-Pybox (**7**)	<5		
8	MeO-Biphep (**8**)	<5		
9	H-MOP(**9**)	<5		



Results and Discussion

1. Reaction Development. *A. Ligand Evaluation.* On the basis of the mechanism depicted in Scheme 1, platinum complexes were avoided in exploratory studies since chiral bidentate ligands were expected to prohibit alkene coordination and insertion reactions that involve d^8 diboryl intermediates. Instead, an initial comparative ligand analysis was conducted with a Rh(I) salt and included a number of symmetric and nonsymmetric bidentate ligands as well as a monodentate ligand structure (Table 1). This survey was executed with *trans*-β-methylstyrene and bis(catecholato)diboron [$B_2(cat)_2$] as the reaction substrates. Each chiral ligand under question was first treated with $(cod)_2RhBF_4$ followed by the diboron reagent in THF at room temperature. Subsequently, the alkene was added and the reaction allowed to stir for 12 h. Oxidative workup was accomplished by

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(16) For the organometallic chemistry of transition-metal boryls, see: Irvine, G. J.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G. R.; Wright, L. J. *Chem. Rev.* **1998**, *98*, 2685.

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(18) Competitive β-hydrogen elimination is catalyst and substrate dependent, see ref 10.

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(20) Bidentate ligands are known to inhibit the Pt-catalyzed diboration of alkynes and the Pd-catalyzed diboration of allenes. See ref 14f and Pelz, N. F.; Woodward, A. R.; Burks, H. E.; Sieber, J. D.; Morken, J. P. *J. Am. Chem. Soc.* **2004**, *126*, 16328.

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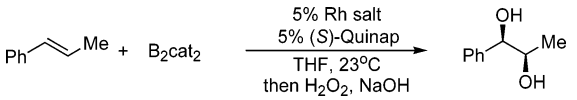
TABLE 2. Analysis of Transition-Metal Salts in the Asymmetric Alkene Diboration Reaction with (*S*)-Quinap



entry	Rh salt	% yield[a]	% ee[b]
1	(nbd)Rh(acac)	71	93
2	(cod)Rh(acac)	43	93
3	(ethylene)Rh(acac)	50	92
4	$(nbd)_2RhBF_4$	56	95
5	$(cod)_2RhBF_4$	24	86
6	$(cod)_2IrBF_4$	<5	

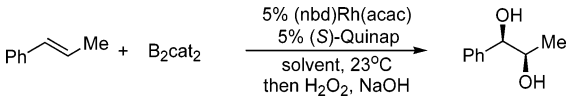
[a] Isolated yield of purified material. [b] Determined by chiral GC analysis.

treatment with basic hydrogen peroxide and the resulting diol analyzed. As the results in Table 1 show, only a few chiral ligands are able to furnish effective diboration catalysts when combined with the rhodium salt. Modification of the metal with Quinap[23] provides the highest diastereo- and enantioselectivity; however, Binap also provides an interesting reaction outcome wherein a significant amount of the anti isomer is formed and delivered in moderate enantiomeric excess.

B. Transition-Metal Salt. Due to the superior selectivity exhibited by Quinap, this ligand was selected for further experimentation. As observed in Table 2, significantly improved yield and selectivity could be achieved by alteration of the transition-metal salt. Whereas the reaction with $(cod)_2RhBF_4$ provided a mediocre yield in the initial survey, when complexed with Quinap the cationic $(nbd)_2RhBF_4$ and neutral (nbd)Rh(acac) provide useful product yields and are the best of those examined. In an effort to understand the nature of the transition-metal−ligand complex that is formed under the reaction conditions, (nbd)Rh(acac) was treated with Quinap and the reaction examined by ^{31}P NMR. While simply mixing the ligand and the metal did not lead to a change in the ^{31}P resonance of the Quinap ligand (−13 ppm), upon addition of 3 equiv of $B_2(cat)_2$, association of Quinap with the metal does occur and provides a number of species with the dominant one resonating at 34.0 ppm ($^1J_{P-Rh}$ = 160 Hz). When the (nbd)Rh(acac)/Quinap-catalyzed reaction is followed by ^{31}P NMR, many new species are apparent with none clearly dominant and none resonating at 34.0 ppm. In contrast, when $(nbd)_2RhBF_4$/Quinap-catalyzed reaction is followed by ^{31}P NMR, two species dominate a handful of minor species, and the minor compound of the pair can also be found in the NMR of the (nbd)Rh(acac)/Quinap-catalyzed process (^{31}P δ = 67.9 ppm, $^1J_{P-Rh}$ = 174.9 Hz). These experiments leave open the possibility that both the neutral and the cationic catalyst provide the same active catalyst under the reaction conditions as one might suspect based on the observations in Table 2.

C. Reaction Solvent. Sequential single-pot reaction sequences that are initiated with asymmetric diboration may be more facile if the diboration reaction can be catalyzed in alternate solvents.[21,22] Therefore, after analysis of the transition-metal salt, the effect of reaction solvent was surveyed. As depicted in Table 3, THF proved to be the most effective solvent for the reaction; however, toluene also afforded modest yields of reaction product. Other solvents such as dichloromethane, ether, dimethoxyethane, and dichloroethane provided the diboration product in comparable optical purity although in diminished yields. Generally, the diboron reagent was much less soluble in these other solvents.

TABLE 3. Examination of Solvent Effects in the Rh−Quinap-Catalyzed Diboration of Alkenes



entry	solvent	time (h)	% yield[a]	syn:anti[b]	% ee[b]
1	THF	12	71	>50:1	93
2	CH_2Cl_2	24	21	34:1	90
3	dichloroethane	12	20	>50:1	92
4	dimethoxyethane	24	15	9.4:1	87
5	toluene	24	35	46:1	87
6	ether	12	17	45:1	89
7	acetonitrile	12	<5		
8	acetone	24	<5		
9	1,4-dioxane	24	27	21:1	83

[a] Isolated yield of purified material. [b] Determined by GC analysis on a permethylated β-cyclodextrin column.

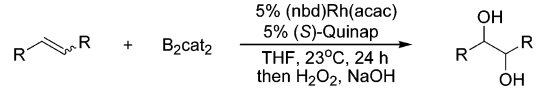
2. Reaction Scope. *A. 1,2-Disubstituted Alkenes.* Unfunctionalized 1,2-disubstituted alkenes participate in the Rh−Quinap-catalyzed diboration reaction with the trans alkene geometry reacting with excellent levels of enantioselectivity. As depicted in Table 4, aromatic substitution is tolerated but not required in the diboration reaction with both stilbene and a substituted styrene providing high levels of enantiocontrol (entries 1 and 2). Internal aliphatic alkenes are optimal reaction substrates with *trans*-5-decene reacting in good yield and excellent enantioselection. As demonstrated with entries 4 and 5, protected hydroxyl functionality is tolerated in the form of silyl ethers; notably, the coordinating functionality present in both MOM ethers and benzyl ethers is inconsequential to the reaction outcome, and good yields and high selectivities result (entries 6 and 7). In contrast to the reactions of trans alkenes, cis alkenes react with varying levels of selectivity. While indene is converted to the derived 1,2-diol in a selective fashion, *cis*-β-methylstyrene provides low selectivity and favors the opposite enantiomer of the reaction product. In contrast, the Rh/Quinap-catalyzed hydroboration of *cis*-β-methylstyrene, as described by Brown, provides higher selection and the same sense of induction as compared to indene.[24]

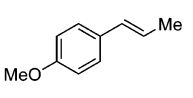
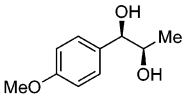
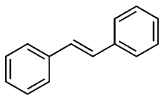
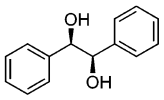
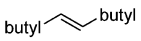
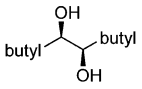
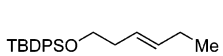
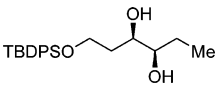
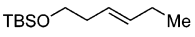
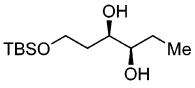
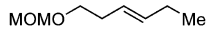
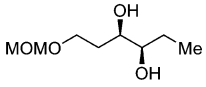
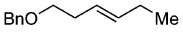
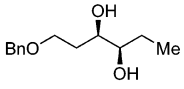
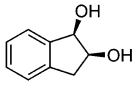
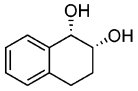
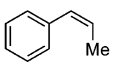
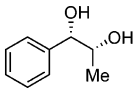
B. Monosubstituted Alkenes. These alkenes are attractive substrates for diboration reactions since the primary and secondary C−B bonds may be differentially functionalized in postreaction derivatization. As depicted in Table 5, this alkene class is also the most challenging in the Rh−Quinap-catalyzed diboration reaction. The reaction rates are significantly higher than with trans alkenes, and the reactions often reach completion in less than 1 h. Simple α-olefins react with mediocre selectivity (ca. 60% ee) when sterically undemanding functionality

(23) (a) Alcock, N. W.; Brown, J. M.; Hulmes, D. I. *Tetrahedron: Asymmetry* **1993**, *4*, 743. (b) Lim, C. W.; Tissot, O.; Mattison, A.; Hooper, M. W.; Brown, J. M.; Cowley, A. R.; Hulmes, D. I.; Blacker, A. J. *Org. Proc. Res. Dev.* **2003**, *7*, 379.

(24) Doucet, H.; Fernandez, E.; Layszell, T. P.; Brown, J. B. *Chem. Eur. J.* **1999**, *5*, 1320.

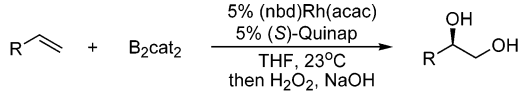
TABLE 4. Rh−Quinap-Catalyzed Diboration of 1,2-Disubstituted Alkenes

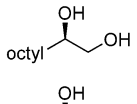
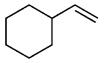
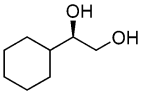
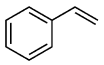
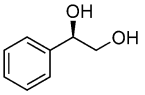
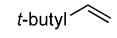
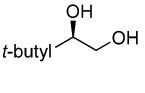
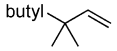
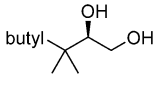
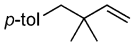
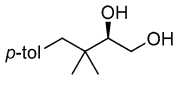
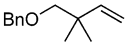
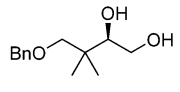
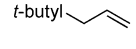
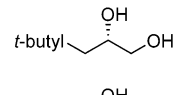
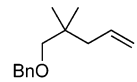
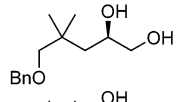


entry	substrate	product[a]	% yield[b]	% ee[c]
1			71	>98
2			48	98
3			76	98
4			77	98
5			62	97
6			53	97
7			68	98
8			68[d]	88
9			72	49
10			61	49

[a] Configuration of reaction products determined by comparison to authentic compounds. [b] Isolated yield of purified material; value is an average of two experiments. [c] Determined by chiral GC or SFC analysis. [d] In addition to the 1,2-diol, this reaction provided 17% 1-indanol.

TABLE 5. Rh−Quinap-Catalyzed Diboration of Monosubstituted Alkenes



entry	substrate	product[a]	time (h)	%yield[b]	%ee[c]
1			6	82	62
2			6	81	59
3			6	68	33
4			6	47	94
5			6	82	95
6			6	74	96
7			6	71	93
8[d]			15	79	61
9			15	64	76
10			15	76	66

[a] Configuration of reaction products determined by comparison to authentic compounds. [b] Isolated yield of purified material; value is an average of two experiments. [c] Determined by chiral GC, HPLC, or SFC analysis. [d] (*R*)-Quinap was used for this experiment.

is present at the allylic carbon (entries 1 and 2), and styrene reacts in a notably nonselective fashion in the Rh−Quinap-catalyzed diboration reaction. The outcome with styrene stands in stark contrast to the selectivity observed in the analogous Rh−Quinap-catalyzed hydroboration reaction (91.5% ee) for which aromatic alkenes are the only selective substrate class.[24] Aliphatic alkenes with an encumbered α-carbon in the form of a quaternary center react with enhanced selectivity, providing product in the range of 93−96% ee (entries 4−7). When comparable quaternary centers are one carbon removed from the alkene, the selectivity is substantially diminished as demonstrated in entries 8−10.

In an effort to improve the stereoselection with monosubstituted alkenes, the (nbd)Rh(acac)/Quinap-catalyzed diboration was examined with alternate diboron reagents. It was expected that with increased steric encumbrance adjacent to the boron atom, improved facial differentiation might result. As depicted in Scheme 2, substituted bis(catecholato)diboron reagents were used in place of $B_2(cat)_2$, and while reactivity was slightly diminished, there was essentially no change in the level of selectivity. It appears that even with diboron **10** in Scheme 2 the substitution is too far removed from the metal center to have a significant impact on selectivity.

C. 1,1-Disubstituted and Trisubstituted Alkenes. Table 6 describes the reaction outcome with 1,1-disubstituted and trisubstituted alkenes, both of which provide a tertiary C−B bond in the reaction intermediate. As observed, the yields in these reactions often suffer and, for 1,1-disubstituted alkenes where the steric bias of the alkene prochiral faces is lessened, the selectivity is expectedly low. With trisubstituted alkenes high enantioselection results and the sense of asymmetric induction

SCHEME 2. Rh−Quinap-Catalyzed Diboration of 1-Decene with Substituted Diboron Reagents

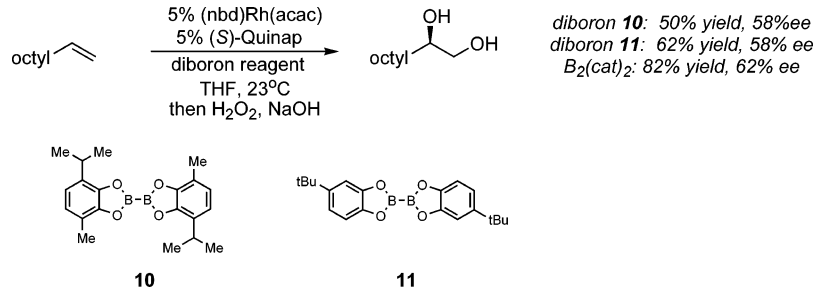
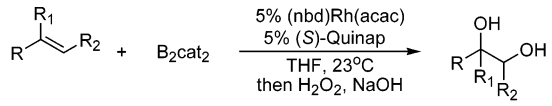
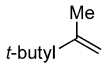
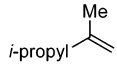
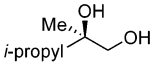
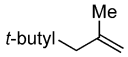
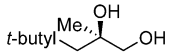
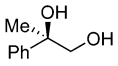
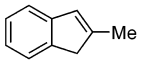
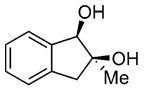
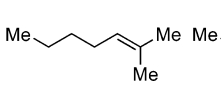
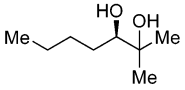


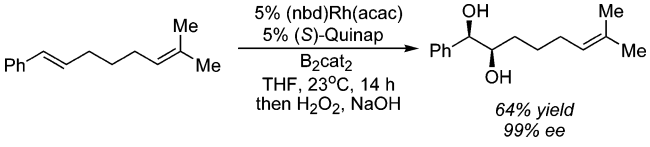
TABLE 6. Rh−Quinap-Catalyzed Diboration of 1,1-Disubstituted and Trisubstituted Alkenes



entry	substrate	product[a]	time	% yield[b]	% ee[c]
1		No reaction	14	<5	-
2			14	58	25
3			14	79	14
4			24	67	46
5			24	17	93
6			24	8	91

[a] Configuration of reaction products determined by comparison to authentic compounds. [b] Isolated yield of purified material; value is an average of two experiments. [c] Determined by chiral GC or SFC analysis.

SCHEME 3. Selective Diboration of a Diene Substrate



is identical to that observed with trans-disubstituted and monosubstituted alkenes.

The reactivity characteristics observed in the tables above suggest that one might observe selective transformation of the less substituted olefin in a diene substrate. To probe such a possibility the diboration reaction in Scheme 3 was executed. As anticipated, steric effects dominate the reaction outcome and the trisubstituted alkene is essentially untouched in the diboration product. The product 1,2-diol may be isolated in good yield and high enantiomeric excess.

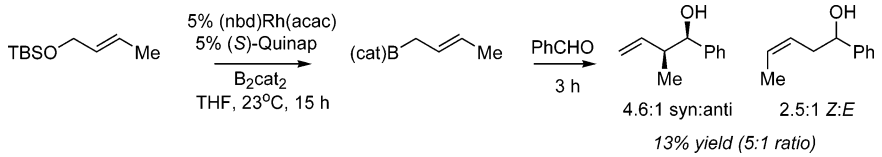
D. Allylic Ethers. Substrates with functionality that may participate in oxidative addition reactions with transition metals are problematic in the alkene diboration reaction. For instance, alkenes that contain allylic ethers or contain aryl halides or triflates do not cleanly provide the 1,2-bis(alkylboronate) upon treatment with $B_2(cat)_2$ and the Rh−Quinap combination. As depicted in Scheme 4, allylic ethers are converted to the corresponding allylboronate when subjected to the asymmetric diboration reaction conditions. This transformation proceeds whether the allylic oxygen atom is protected as an ester, an aryl ether, or a silyl ether. While this transformation has been documented for Pd catalysts with bis(pinacolato)diboron,[25] it is heretofore unknown with Rh catalysts. Substrates containing aryl halides and triflates provide either low reaction yields or the product of alkene hydroboration when subject to the alkene diboration reaction (data not shown).

3. Stereochemical Model. Experiments that provide insight into the mechanism of the rhodium−Quinap-catalyzed asymmetric diboration have not yet rigorously established one series of elementary steps as that responsible for diboration catalysis. However, available observations are consistent with a mechanism involving oxidative addition, olefin insertion, and reductive elimination as described for the nonasymmetric processes presented in Scheme 1. The first compelling evidence for such a cycle is that the reaction products from the Rh−Quinap-catalyzed diboration arise from net syn addition across the alkene. In contrast, the anti diastereomer which arises during Rh−Binap-catalyzed diboration of *trans*-β-methylstyrene provides evidence that alternate pathways may operate. The origin of the anti diastereomer that is produced with Rh−Binap was elucidated by examination of this catalyst with indene as the substrate. As depicted in Scheme 5, this experiment provides a mixture of the expected 1,2-diol but also *cis*-1,3-indanediol (**13**) and 1-indanol (**14**) as the reaction products. A reasonable sequence of events that would lead to such an outcome involves coordination and insertion of the alkene with a bis(boryl)rhodium complex to give **15**. Reductive elimination from **15** would give the observed 1,2-diol **12**, while β-hydrogen elimination from **15** would give **16**. Intermediate **16** might undergo reinsertion/reductive elimination to give 1,3-diol **13**, or it might dissociate the allylboronate to give a hydrido(boryl)-rhodium complex which could affect hydroboration of the starting alkene to furnish **14**.[26]

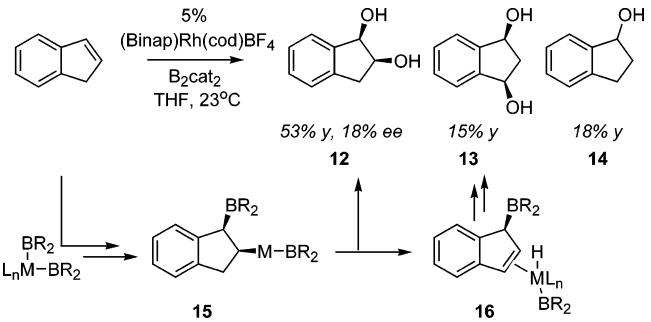
Relative to the Rh−Binap-catalyzed reaction, the diboration of indene with the (nbd)Rh(acac)/Quinap catalyst

(25) (a) Ishiyama, T.; Ahiko, T.; Miyaura, N. *Tetrahedron Lett.* **1996**, *37*, 6889. (b) Ahiko, T.; Ishiyama, T.; Miyaura, N. *Chem. Lett.* **1997**, 811.

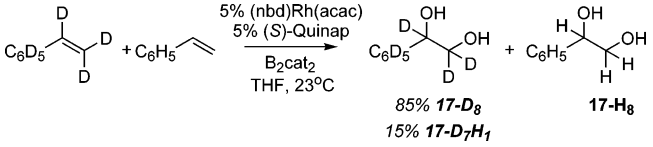
SCHEME 4. Reaction of an Allylic Ether under Rh-Catalyzed Diboration Conditions



SCHEME 5. Rh−Binap-Catalyzed Diboration of Indene



SCHEME 6. Crossover in Rh−Quinap-Catalyzed Diboration of Deuteriostyrne and Protiostyrene



provides less 1-indanol (4:1 **12:14**) and no 1,3-diol **13**. This observation suggests that β-hydrogen elimination pathways are less operative with this catalyst. To further substantiate this claim, a mixture of styrene and styrene-d_8 was subjected to the Rh−Quinap-catalyzed diboration. Mass spectral analysis of the resulting 1,2-diol **17** showed that in addition to **17-D**$_8$ a small amount of **17-D**$_7$H$_1$ is also present. Production of **17-D**$_7$H$_1$ is consistent with the observations above wherein β-hydrogen elimination/hydroboration compete with alkene diboration. As expected, nonlabeled compound **17-H**$_8$ was also present; however, it was not possible to determine the amount of **17-D**$_1$H$_7$ present as this compound has the same mass as the ^{13}C isotopomer of **17-H**$_8$, Scheme 6. Collectively, the observations with indene and labeled styrene suggest that β-hydrogen elimination/hydroboration processes, at the very most, only provide a minor pathway toward generation of the reaction product.[27]

As described above, NMR analysis of metal−ligand complexes has not proven informative. As an alternative means to learn more about the nature of the active catalyst in alkene diboration reactions we studied the relationship between ligand enantiopurity and product enantiopurity.[28] As depicted in Figure 1, nonlinear effects are absent in the Rh−Quinap-catalyzed diboration and

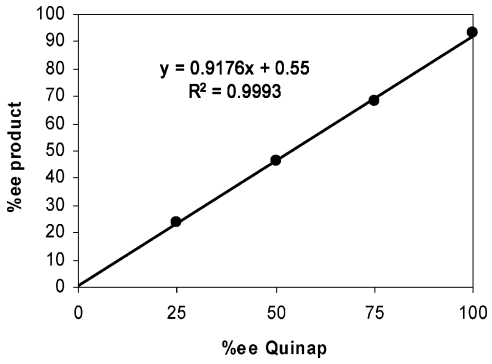
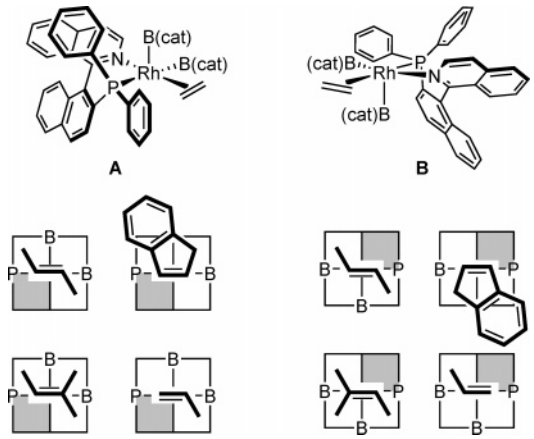


FIGURE 1. Correlation between %ee Quinap ligand and %ee diboration product.

SCHEME 7. Predictive Model for Rh−Quinap-Catalyzed Alkene Diboration



a near-perfect correlation exists between the optical purity of the ligand and that of the product. These experiments are highly suggestive of a catalyst which is monomeric with a single ligand structure on the metal.

Stereochemical models for the Rh−Quinap-catalyzed alkene diboration reaction are depicted in Scheme 7. These models are based on the assumption that the mechanism in Scheme 1 operates and are also based on the crystallographic analysis of the Quinap ligand coordinated to ruthenium and palladium centers.[29] In model A it is suggested that after oxidative addition of $B_2(cat)_2$ to Rh(I) the alkene coordinates to the Rh(III) center opposite the weaker trans-effect atom (nitrogen) and insertion occurs into the equatorial Rh−B bond as it is weakened by the strong trans-influence phosphine ligand.[30] In model B the anionic boryl ligand is trans to the less basic atom of the Quinap ligand, leading to a

(26) Dissociation of a hydrido(boryl)rhodium structure from **16** implies that an allylboronate should be generated. We have not detected this compound, although it is reasonable to anticipate that it might be protonated rapidly upon aqueous oxidative workup.

(27) At this point we have been unable to rule out a mechanism involving insertion of an alkene into a Rh(I) boryl complex followed by oxidative addition to $B_2(cat)_2$ and reductive elimination of the bis(boronate) product. Crossover experiments would provide this information; however, we have found that $B_2(cat)_2$ and $B_2(4\text{-}t\text{-BuCat})_2$ undergo noncatalyzed exchange of the catechol ligands, thereby precluding this experiment.

(28) For reviews, see: (a) Blackmond, D. G. *Acc. Chem. Res.* **2000**, *33*, 402. (b) Girard, C.; Kagan, H. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 2922.

(29) (a) Alcock, N. W.; Brown, J. M.; Hulmes, D. I. *Tetrahedron: Asymmetry* **1993**, *4*, 743. (b) Faller, J. W.; Grimmond, B. J. *Organometallics* **2001**, *20*, 2454.

more stable and perhaps more populated coordination geometry. Since the Quinap ligand provides a pseudo-C_2-symmetric steric environment about the metal center, both models A and B lead to the same set of stereochemical predictions. If quadrant diagrams[31] are used to demarcate the steric environment surrounding the coordinated alkene, then the lower left quadrant is occupied by the equatorial phenyl group of the PPh_2 element in model A and the top right quadrant is occluded by the isoquinoline in model B. On the basis of these diagrams it can be predicted that trans- and trisubstituted alkenes should react in a selective fashion and favor the observed product enantiomer. Similarly, indene and 2-methylindene should react selectively assuming that regioselective alkene insertion occurs to provide the more stable benzylic C−Rh bond. With monosubstituted and 1,1-disubstituted alkenes the initial insertion might be expected to provide the less hindered primary C−Rh bond. One would therefore predict less enantiofacial control in reactions of monosubstituted and 1,1-disubstituted alkenes since there is not an obvious steric bias between the quadrants which are opposite the chiral ligand. This model does not readily predict the low level of stereoselection with styrene nor does it provide a rationale for the turnover in selectivity with dihydronaphthalene relative to indene.

Conclusion

The enantioselective diboration of alkenes can be catalyzed by chiral rhodium−Quinap complexes, and the reaction is effective for a number of alkene substrates. The sense and levels of stereoinduction can be predicted in a reliable fashion for many alkene substrates. Current experiments are aimed at gaining a better understanding of the reaction mechanism and developing improved ligand structures based on the stereochemical hypotheses developed herein.

(30) For an excellent discussion of the steric and electronic properties of amines in relation to phosphines, see: Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 497.

(31) Gladyz, J. A.; Boone, B. J. *Angew. Chem,. Int. Ed. Engl.* **1997**, *36*, 551.

Experimental Section

Representative Procedure for the Catalytic Diboration of *trans*-β-Methylstyrene. An oven-dried 20 mL vial equipped with a stir bar was charged with 3.7 mg (12.5 μmol) of (bicyclo[2.2.1]hepta-2,5-diene)-(2,4-pentanedionato)rhodium-(I) [(nbd)Rh(acac)], 5.5 mg (12.5 μmol) of (*S*)-Quinap, and 0.5 mL of THF under an inert atmosphere of argon in a drybox. The resultant yellow solution was stirred for 5 min. After this time 65.4 mg (0.28 mmol) of bis(catecholato)diboron was added to the solution under argon. The solution turned immediately from yellow to dark brownish-red. The solution was allowed to stir for 5 min. After this time 29.5 mg (0.25 mmol) of *trans*-β-methylstyrene was added to the solution under argon. The vial was sealed with a screw cap and removed from the drybox, where the solution was allowed to stir for 14 h at ambient temperature. After this time the mixture was cooled to 0 °C and 0.4 mL of 3 M NaOH and then 0.4 mL of 30% H_2O_2 were added (dropwise with caution) under nitrogen. The solution was allowed to stir at ambient temperature for 3 h. The solution was then quenched with 0.5 mL of saturated aqueous $Na_2S_2O_3$ and 5 mL of 1 M NaOH. The mixture was extracted with ethyl acetate (3 × 10 mL), and the combined organic layers were washed with brine (1 × 10 mL). The organic layers were then dried over anhydrous $MgSO_4$ and filtered, and the solvent was removed by rotary evaporation. The crude material was purified by silica gel chromatography (1:1 hexanes:ethyl acetate) to provide 27.2 mg (71%) of pure (*1R,2R*)-1-phenylpropane-1,2-diol. R_f = 0.24 (silica gel, 1:1 hexanes:ethyl acetate). IR (neat, ν cm^{-1}): 3384, 1455, 1038. ^1H NMR: δ 7.25−7.42 (5H, m), 4.36 (1H, d, J = 7.6 Hz), 3.85 (1H, qd, J = 7.2 Hz, 6.4 Hz), 2.44 (2H, br s), 1.05 (3H, d, J = 6.4 Hz). ^{13}C NMR: δ 141.0, 128.5, 128.2, 126.8, 79.5, 72.2, 18.8. HRMS (FAB) Calcd for $C_9H_{16}NO_2$ $(M + NH_4)^+$: 170.1181. Found: 170.1177. Chiral GLC (β-dex, Supelco, 140 °C, 20 psi): major isomer (1*R*,2*R*) 51.6 min; minor isomer (1*S*,2*S*) 49.7 min.

Acknowledgment. Support from the NIH (NIGMS: R01-GM59417) is gratefully acknowledged.

Supporting Information Available: Complete experimental procedures, characterization data (^1H and ^{13}C NMR, IR, and mass spectrometry), enantiomeric purity data (chiral GC, HPLC, SFC), and structure proofs (authentic syntheses). This material is free of charge via the Internet at http://pubs.acs.org.

JO051651M