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Metal promoted asymmetry in the 1,2-diboroethylarene synthesis: diboration versus dihydroboration

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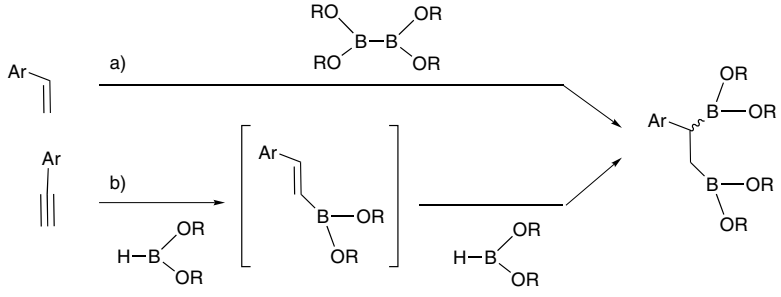
Abstract—Metal catalysed addition of diboranes to vinylarenes produces the desired 1,2-bis(boronate)ester and mono(boronate)esters as by-products. Their relative rate is a sensitive function between the nature of the catalytic system and the electronic effects of the substrate, that influences the mechanistic steps of the catalytic cycle. However, asymmetry is only induced as moderate enantiomeric excess values, providing an enantioface differentiation, between the bis- and mono(boronate)esters. Alternatively, the method based on the catalytic asymmetric dihydroboration/oxidation of alkynes as diphenylacetylene can provide 1,2-diphenyl-1,2-ethanediol (hydrobenzoin) with a selectivity of 68% mainly as the *erythro* isomer.

1. Introduction

The addition of two boryl units onto adjacent carbons is becoming increasingly important for the efficient assembly of homo- and hetero-difunctional molecular structures.[1] The diboration (Scheme 1a) and dihydroboration (Scheme 1b) of alkenes and alkynes, respectively, are attractive and straightforward strategies. Whereas, non-catalysed diborane-addition reactions are limited to the use of highly reactive tetrahalodiboranes,[2] the mediation of transition metal catalysts allows the use of less reactive[3] and easier-to-handle tetraalkoxy- and tetraaryloxydiboranes. Unlike 1,2-diboro addition reactions, *gem*-diboro adducts are mainly produced from both the uncatalysed[4] and metal-mediated[5] in situ dihydroboration of unsaturated substrates. However, alkenylboronic esters, previously isolated from the hydroboration of terminal alkynes, can be subjected to a second catalytic reaction to provide 1,2-diboryl derivatives.[6] Although they have been much less studied, enantioselective routes towards the diborane adduct have been established[6,7] by applying chiral ligands on the catalytic system. However, further improvements in catalyst efficiency are required because yield and selectivity are still low.

Herein we report our interest in determining the nature of the side reactions and by-products produced during



Scheme 1.

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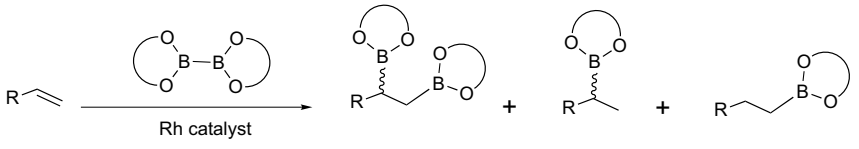
the catalytic asymmetric diboration of vinylarenes and extend our study to attempt the first example of an in situ catalytic asymmetric dihydroboration of internal alkynes.

2. Results and discussion

A certain level of enantioenrichment (ee = 33%), has been described in the asymmetric diboration of styrene **1a** with bis(catecholato)diboron **2** by means of the catalytic system [Rh(nbd)acac]/(*S*)-Quinap.[7] Moreover, the reported isolated yield of purified material was moderate (68%), and the remaining mass balance described as unconverted starting material. When we reproduced this reaction under identical conditions (Scheme 2), we found that whereas the enantioselectivity was roughly as reported, the conversion of the substrate was almost complete and the formation of hydroborated products became significant (Table 1, entry 1). These findings are in agreement with the well-known studies by Baker et al.,[8] Marder and co-workers[8,9] and Marder and Norman[9] in which, depending on the rhodium(I) catalytic system used, a range of products from mono-, bis- and tris-boronated derivatives, were observed. A plausible explanation, from a mechanistic point of view, suggests that the first step is likely to be an oxidative addition of B–B in the diborane reagent[10] to the metal, leading to metal–diboryl complex (Scheme 3, path a). However, the desired 1,2-bis(boronate)ester seems to arise from alkene insertion into one M–B bond followed by B–C reductive elimination involving the second boryl ligand (Scheme 3, paths b–b′), the alkenyl and alkylboronate esters could be produced as a result of a competitive β-H-elimination (Scheme 3, paths c–c′, d–d′). Even the addition of achiral monophosphine to block any vacant coordination site around the rhodium, involving an unfavourable β-H-elimination step, did not improve selectivity (Table 1, entry 2).

At this point, we could infer two things from our initial catalytic results with [Rh(nbd)acac]/(*S*)-Quinap. Firstly, the enriched enantiomer in the 1,2-bis(boronate)ester was *R* while the enriched enantiomer in the 1-phenylethylboronate ester was *S*. Secondly, the standard catalytic asymmetric hydroboration of styrene provided much higher ee values (88%)[11] under similar reaction conditions than as a side hydroboration reaction produced. We should point out that the P,N-ligand (*S*)-Quinap does not induce as much asymmetry in the 2-phenylethylboronate obtained as by-product in diboration as in standard hydroboration, probably because a different chiral metal (β-borylalkyl) species is involved in the catalytic cycles.

To analyse how much the relative rates of B–C reductive elimination versus β-hydride elimination, are sensitive functions of the chiral ligand, new catalytic 1,2-diborations of styrene were performed with [Rh(nbd)acac] modified with (*R*)-Binap and (*S*,*S*)-BDPP. Selectivity on the 1,2-bis(boronate)ester was significantly reduced with the ligand *R*-Binap, which chelates with rhodium



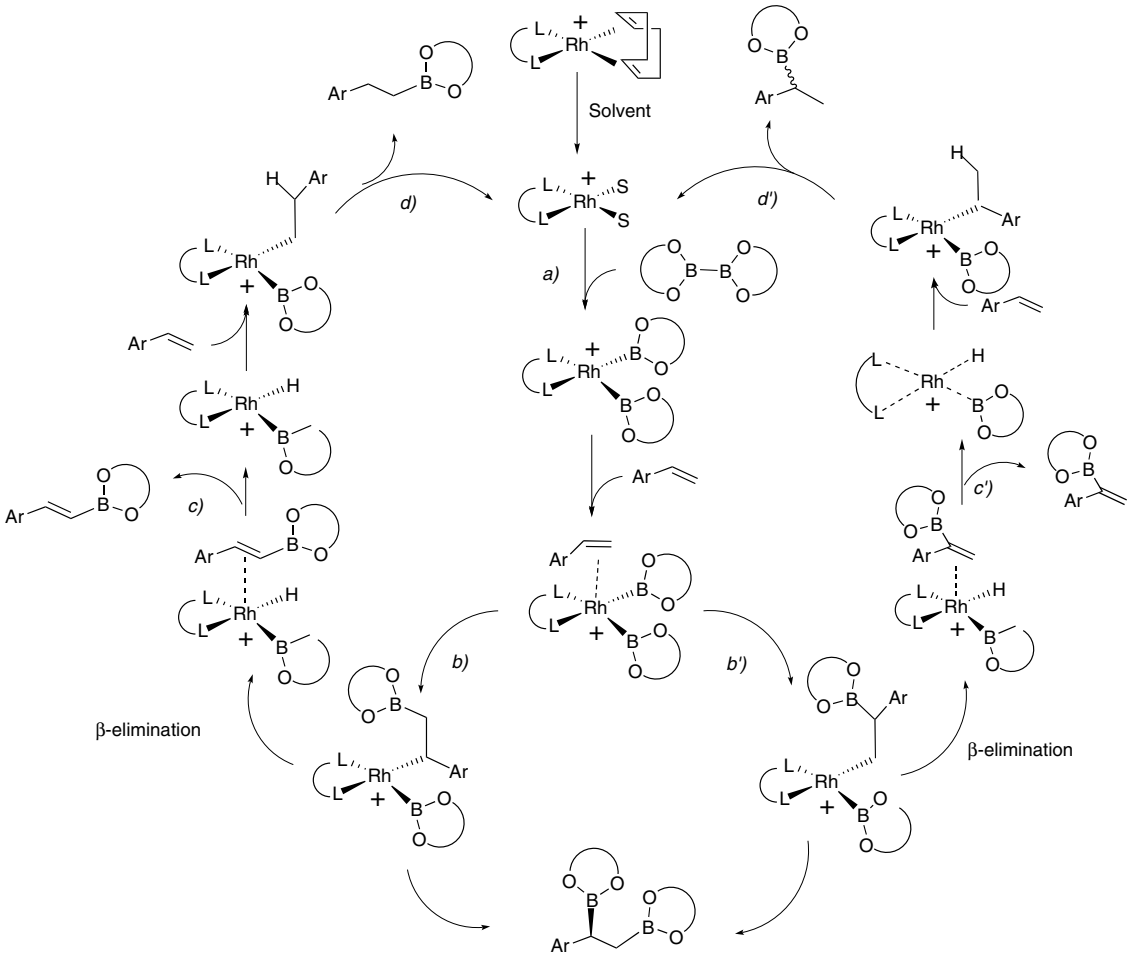
1a: R= C_6H_5
1b: R= *p*-MeO-C_6H_4
1c: R= *p*-F-C_6H_4
1d: R= C_6H_{11}

Scheme 2.

Table 1. Catalytic asymmetric 1,2-diboration reaction of vinylarenes with bis(catecholato)diboron[a]

Entry	Substrate	Catalytic system	Conversion[b] (%)	% **3**[b] (% ee)[c]	% **4**[b] (% ee)[c]	% **5**[b]
1	**1a**	[Rh(nbd)acac]/(*S*)-Quinap	90	76 (35*R*)	24 (34*S*)	—
2	**1a**[d]	[Rh(nbd)acac]/(*S*)-Quinap	78	70 (37*R*)	27 (33*S*)	3
3	**1a**	[Rh(nbd)acac]/(*R*)-Binap	99	21 (21*R*)	69 (3*S*)	10
4	**1a**	[Rh(nbd)acac]/(*S*,*S*)-BDPP	95	17 (16*R*)	68 (2*S*)	14
5	**1a**	$[Rh(nbd)_2]BF_4$/(*S*)-Quinap	95	55 (35*R*)	40 (47*S*)	5
6	**1a**	$[Rh(cod)_2]BF_4$/(*S*)-Quinap	89	66 (36*R*)	34 (41*S*)	—
7	**1a**	$[Rh(\mu\text{-Cl})(nbd)]_2$/(*S*)-Quinap	92	68 (35*R*)	25 (40*S*)	7
8	**1b**	[Rh(nbd)acac]/(*S*)-Quinap	77	82 (26*R*)	11 (—)	7
9	**1c**	[Rh(nbd)acac]/(*S*)-Quinap	58	58 (20*R*)	36 (45*S*)	6
10	**1d**	[Rh(nbd)acac]/(*S*)-Quinap	100	78 (54*R*)	7 (ND)	15

[a] Standard conditions: substrate/bis(catecholato)diboron/Rh complex/chiral ligand = 1/1.1/0.05/0.05; solvent: THF; *T*: 25 °C; *t*: 15 h.
[b] Conversion and selectivity calculated by ^{1}H NMR.
[c] Enantiomeric excess determined by GC with chiral column, as derivated alcohols for **4** and **5**, and derivated acetal for **3**.
[d] Addition of 5 mol % of PPh_3.



Scheme 3.

to form a seven-membered ring (Table 1, entry 3). We observed a similar trend to that using the bidentate ligand DPPB in the [Rh(L–L)acac]/B_2cat_3—catalysed diboration of alkenes.[12] However, not only does the size of the bite angle seem to influence the selectivity of the reaction, because the use of (*S*,*S*)-BDPP, which as (*S*)-Quinap also forms six-membered ring with metal, provided poor selectivities towards the 1,2-diborated product (Table 1, entry 4). Asymmetry induced by both P,P-bidentate ligands, diminishes slightly in the diborated product and significantly in the 2-phenylethylboronate ester. We should point out that the 1,2-diborated product obtained from both chiral complexes modified with (*S*)-Quinap and (*R*)-Binap, mainly provided the same (*R*)-enantiomer. This contrasts substantially with the trend observed in the hydroboration/oxidation of styrene, where the Rh/(*S*)-Quinap catalytic system provided the (*S*)-1-phenylethanol, while the Rh/(*R*)-Binap catalytic system favoured the (*R*)-enantiomer.[11]

We demonstrated the generality of the asymmetric diboration reaction by carrying out the 1,2-addition of bis(catecholato)diboron on styrene, with cationic and neutral precursor of rhodium catalyst modified with (*S*)-Quinap (Table 1, entries 5–7). The results were similar to those obtained with [Rh(nbd)acac]/(*S*)-Quinap, although selectivity on the diborated product seemed to be somewhat sensitive to the nature of the precursor. The electronic factors in the substrate usually alter as much as the steric factors of the catalyst, so we studied how different the aryl substituents would affect chemo- and enantioselectivity.

The electron-rich and electron-deficient vinylarenes, *p*-methoxystyrene and *p*-fluorostyrene, respectively, produced similar but low enantioselectivities (Table 1, entries 8 and 9). The chemoselectivity towards the 1,2-diborated product was the most satisfactory (82%), when the electron-releasing aryl substituent was used on the styrene substrate. Noting that during alkene insertion into Rh-boryl complex, chemo- and enantioselection were dependent on alkene electronics, we reasoned that aliphatic 1-alkenes might exhibit different selectivity patterns from those of aromatic olefins. Table 1, entry 10 shows that vinylcyclohexane was mainly converted into the desired 1,2-bis(boronate)ester with moderate enantiomeric excess (54%). However the percentage of terminal hydroborated products was twice that of the branched hydroborated product.

Attempts to inhibit the competitive β-hydride elimination process has been covered by different strategies mainly related to the nature of the catalyst,[8,12] and less related to the nature of the diborating reagent. Miyaura

and co-workers[13] reported the addition of bis(pinacolato)diboron to terminal alkenes using a catalytic amount of $Pt(dba)_2$ at 50 °C. Though cleaner 1,2-diboration addition was observed, the base-free Pt system could not be modified with chiral ligands.

Bearing these precedents in mind, we studied how tetraalkoxydiboranes other than bis(catecholato)diboron (Fig. 1), influence the 1,2-diboration addition to styrene using the catalytic system [Rh(nbd)acac]/(*S*)-Quinap. Table 2 shows that chemoselectivity towards the desired 1,2-bis(boronate)ester was low and that enantioselectivity was null when bis(neopentylglycolato)diboron **6** and bis(hexyleneglycolato)diboron **7**, were used as diborating reagents (Table 2, entries 1 and 2). However, both reagents favoured the formation of the branched hydroborated by-product, but asymmetric induction was also null. In an attempt to increase enantioselectivity along this model reaction, we performed a double asymmetric induction using the chiral catalytic system [Rh(nbd)acac]/(*S*)-Quinap and chiral diborating reagents.

As Table 2 shows, when bis(diethyl-D-tartrateglycolato)diboron **8** and bis(diisopropyl-D-tartrateglycolato)diboron **9** were involved in the reaction, enantiomeric excesses were only 17% and 14%, respectively (Table 2, entries 3 and 4). Note that in these cases the enantioenriched mixture was on the (*S*)-enantiomer rather than on the favoured (*R*)-enantiomer formed with bis(catecholato)diboron. The change in the main enantiomer must be due to the chiral diborane reagent, as is seen by the reactivity when the catalytic system was not modified with the (*S*)-Quinap (Table 2, entry 5). As far as enantioselectivity is concerned, the chiral diborane reagent bis((+)-pinanediolato)diboron **10** showed a similar behaviour on the 1,2-diboration of *p*-methoxystyrene and vinylcyclohexane (Table 2, entries 6–8). These results are comparable to those of the platinum catalysed diboration of terminal alkenes with other chiral diboranes,[14] although isolated yields of the 1,2-diborated product were higher with platinum than with rhodium as the metal centre of the catalytic system.

As an alternative to the synthetic method, we became interested in performing the dihydroboration/oxidation of internal alkynes with bis(organo)boranes in the presence of the rhodium catalytic system modified with (*S*)-Quinap, in order to explore the viability of the chiral 1,2-diol adduct formation. In particular, we focused on the synthesis of the hydrobenzoin-type molecule, because the enantiomerically pure hydrobenzoin has proven to be a very useful chiral auxiliary[15] and ligand,[16,17] for stereoselective organic synthesis. These diols, which were previously accessible only through kinetic resolution,[18] can now be obtained by the dihydroxylation of olefins,[19] the reduction of benzyls[20] or via carbon–carbon bond formation.[21] However, to the best of our knowledge, nobody has yet studied the enantioselective synthesis of hydrobenzoin through the catalytic asymmetric dihydroboration/oxidation of the diphenylacetylene with boranes such as hydroboration reagents.

We therefore focused on the dihydroboration/oxidation reaction of the internal alkyne diphenylacetylene. We began by examining the catalytic properties of the rho-

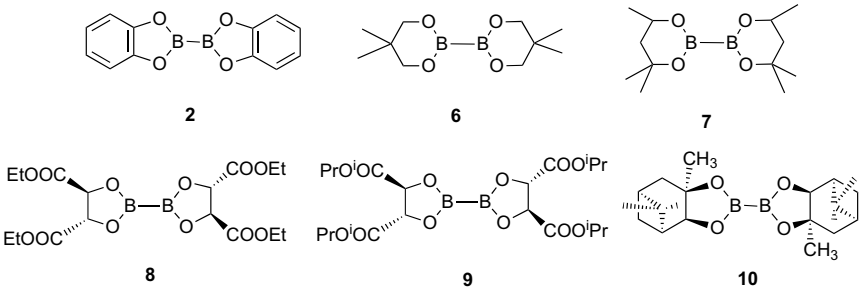


Figure 1.

Table 2. Catalytic asymmetric 1,2-diboration reaction of vinylarenes with [Rh(nbd)acac]/(*S*)-Quinap[a]

Entry	Substrate	Diborane reagent	Conversion[b] (%)	% **3**[b] (% ee)[c]	% **4**[b] (% ee)[c]	% **5**[b]
1	**1a**	Bis(neopentylglycolato)diboron, **6**	95	39 (—)	61 (—)	—
2	**1a**	Bis(hexyleneglycolato)diboron, **7**	36	22 (—)	78 (5*S*)	—
3	**1a**	Bis(diethyl-D-tartrateglycolato)diboron, **8**	60	17 (17*S*)	83 (—)	—
4	**1a**	Bis(diisopropyl-D-tartrateglycolato)diboron, **9**	100	20 (14*S*)	80 (—)	—
5[d]	**1a**	Bis(diisopropyl-D-tartrateglycolato)diboron, **9**	50	12 (23*S*)	88 (—)	—
6	**1b**	Bis((+)-pinanediolato)diboron, **10**	80	36 (14*S*)	64 (—)	—
7[d]	**1b**	Bis((+)-pinanediolato)diboron, **10**	100	25 (15*S*)	75 (ND)	—
8	**1d**	Bis((+)-pinanediolato)diboron, **10**	100	32 (50*S*)	3 (—)	65

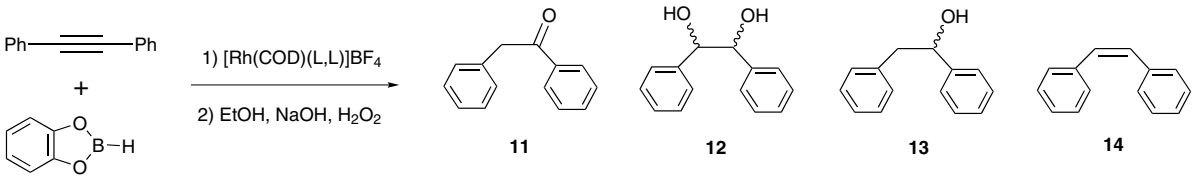
ND: not determined.

[a] Standard conditions: substrate/bis(organo)diboron/Rh complex/chiral ligand = 1/1.1/0.05/0.05; solvent: THF; *T*: 25 °C; *t*: 15 h.

[b] Conversion and selectivity calculated by ^{1}H NMR.

[c] Enantiomeric excess determined by GC with chiral column, as derivated alcohols for **4** and **5**, and derivated acetal for **3**.

[d] Catalytic system based on [Rh(nbd)acac].



Scheme 4.

dium complex [Rh(cod)(dppp)]BF_4 in THF as solvent, with an equimolecular amount of catecholborane (Scheme 4). Although we expected ketone **11** to be the major product obtained, this was in fact the diol diphenyl-1,2-ethanediol **12** (hydrobenzoin) (Table 3, entry 1). Therefore, a double amount of borane reagent (2.2 equiv) guaranteed a higher conversion. However, not only did the conversion significantly improve, but selectivity towards the diol **12** also increased to 60% (Table 3, entry 2).

Other by-products (Scheme 4), were observed as a result of competitive catalytic reactions, such as hydrogenation. These secondary reactions may be related to the degradation of catecholborane in the reaction media, which depends on the nature of the phosphine ligands, the rhodium complex and the solvent. It seems that catecholborane breaks down to afford a variety of boron products such as the diborane **15** plus metal hydro species such as [$Rh(H_2)$(L,L)][$B(cat)_2$] (Scheme 5).[22] The production of the rhodium dihydro species may be responsible for the formation of hydrogenated products. The ^{11}B NMR spectra determined during the dihydroboration reaction, showed two broad signals at $\delta(^{11}B) = 33.0$ ppm and $\delta(^{11}B) = 21.5$ ppm, in agreement with the alkylboronate products and compound **15**, respectively.

On the basis of these observations, we suggest that diphenylacetylene was involved in competitive hydroboration and/or hydrogenation reactions, as illustrated in Scheme 6. While the dihydroboration of diphenylacetylene provided the desired hydrobenzoin **12**, hydroboration followed by hydrogenation of the intermediate gave 1,2-diphenylethanol **13**. Alkene **14** could also be formed from the catalytic hydrogenation of the alkyne.

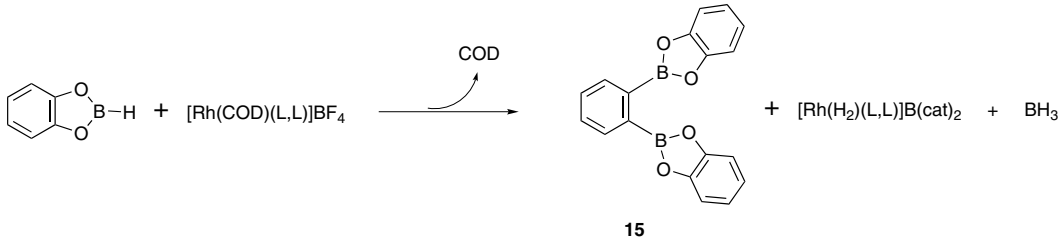
As far as the catalytic asymmetric dihydroboration/oxidation of diphenylacetylene is concerned, the chiral complex [Rh(cod)(*S*,*S*)-bdpp]BF_4 with catecholborane provided conversion and selectivity (Table 3, entry 3) similar to those of [Rh(cod)dppb]BF_4. However diphenyl-1,2-ethanol **12** was characterised mainly as the *erythro* compound, not the expected *threo*. Unfortunately, even modifying the rhodium complex with other chiral ligands, such as Quinap and Binap, did not change this trend towards the formation of the *erythro* compound.

Also, the formation of diol **12** was not favoured with the latter bidentate ligands (Table 3, entries 4 and 5). One explanation for the formation of the *syn*-diol could be that the alkenylboronate ester isomerises from the *cis* to the *trans* isomer, because of the favoured β-H-elimination. The *trans* isomer could then be transformed into the *syn* diboronate during the second catalytic

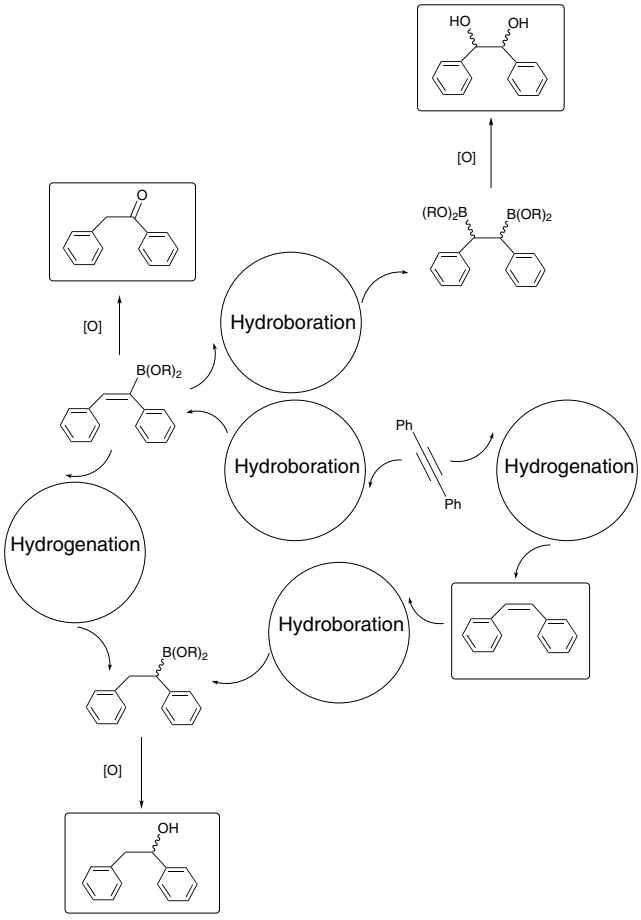
Table 3. Catalytic asymmetric dihydroboration of diphenylacetylene with [Rh(cod)L,L]BF_4 and catecholborane[a]

Entry	L,L	Conversion[b] (%)	% **11**[b]	% **12**[b] (% *erythro*:*threo*)[c]	% **13**[b]	% **14**[b]
1[d]	dppp	37	17	50	25	8
2	dppp	98	3	60	33	3
3	(*S*,*S*)-bdpp	98	4	68 (96:4)	26	2
4	(*S*)-Quinap	78	68	17	15	—
5	(*R*)-Binap	63	15	31 (88:12)	31	23

[a] Standard conditions: substrate/catecholborane/Rh complex/chiral ligand = 1/2.2/0.01/0.01; solvent: THF; *T*: 25 °C; *t*: 2 h.
[b] Conversion and selectivity calculated by ^1H NMR.
[c] Ratio *erythro*/*threo* determined by HPLC, in a chiral column Chiralcel OJH.
[d] Substrate/catecholborane/Rh complex/chiral ligand = 1/1.1/0.01/0.01.



Scheme 5.



Scheme 6.

hydroboration. In summary, we have shown that chemoselectivity in catalytic diboration is sensitive to the nature of the catalyst and to the electronics of the substrate. Moderate enantioselectivity is achieved in 1,2-bis(boronate) and 2-phenylethylboronate esters, but with opposite enantioface. Two consecutive in situ hydroboration/oxidation of alkynes, provides the *syn*-diol derivative with quantitative conversion and selectivity.

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