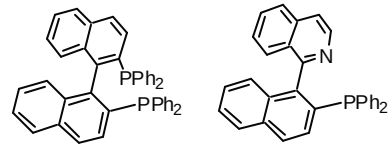
Chapter 2

Catalytic asymmetric hydroboration reaction of vinylarenes

Knowledge of the catalytic cycle of a reaction, makes it possible to understand the activity and selectivity of the catalytic system and the role of the substrates and reagents. For this reason, it is necessary to make an effort to find out more about the reaction mechanism. Unfortunately, this is not an easy task and it is sometimes difficult to acquire date, partly because of the low stability of intermediates. This chapter attempts to rationalise the unpredictability of the transition metal-catalysed asymmetric hydroboration of vinylarenes when the following elements are varied: the electronic nature of the precursor catalyst ([M(cod)(L,L)]BF_4, [M(μ-Cl)(cod)]$_2$/(L,L)), the ligand ((L,L)= (R)-Binap and (R)-Quinap), the metal (M=Rh and Ir) and the hydroborating reagent (catecholborane, pinacolborane). In addition, we investigate the origin of regio- and stereoselectivity on basis to multinuclear NMR spectroscopic studies in agreement with studies based on DFT calculations and QM/MM strategies [1].

1. Introduction

The catalytic asymmetric hydroboration reaction provides a way of transforming alkenes into many different types of C*-X and C*-R bonds via the optically enriched organoboron adduct C*-B. Burgess and Ohlmeyer developed the first catalytic asymmetric hydroboration of olefins in 1988, using rhodium catalyst complexes modified with various diphosphine chiral ligands [2]. However, the potential power of asymmetric catalysts for synthesizing added-value products justifies its development, which is of central importance in modern science and technology [3]. Stereochemical control is derived from the reagent rather than from the catalyst in very few cases. Only, when a reagent is readily and economically available in enantiomerically pure form, does reagent-controlled asymmetric catalysis become a reasonable objective [4]. Generally, asymmetric catalysts are based on transition metal complexes bearing chiral ligands [5]. Homotopic atropoisomeric-type ligands such as Binap (**25**) (Figure 1) [6], which are extremely valuable in a number of reactions, and heterotopic ligands, such as the (P,N) ligand Quinap (**28**) [7], (Figure 1), have made efficient enantioselective synthesis possible in several homogeneous catalytic reactions. Nevertheless, there is no general solution for dealing with asymmetric transformation, probably because of the dramatic effect on the enantioselectivity of the steric and/or electronic properties of the ligand, substrate and reagent.



25 **28**

Figure 1

The catalytic asymmetric hydroboration reaction of vinylarenes can occur with regiochemical and enantiochemical control [8] to give the corresponding chiral 2-aryl boronate esters. But this reaction is not an exception and, the stereoselectivity

depends mainly on the structure and electronic nature of the ligand coordinated to the metal in the catalytic complex, the substrate, and the hydroborating reagent. The effects provided by the structure of the ligand and the nature of the aryl substituents on the vinylarenes have been studied in an attempt to predict the relative importance of the steric and electronic effects [9], [10]. These studies have provided several conclusions that must be taken into account. One of them, suggests that if heterotopic P,N ligands [8b], [9], [11] modify the rhodium complexes, the enantioselectivity is higher than when homotopic P,P ligands are used [8a]. In addition, the cationic rhodium complexes modified with heterotopic P,N ligands in the asymmetric induction of the hydroboration of a model vinylarene such as styrene may or may not be temperature dependent [8e], [9], [11]. Finally, the electronic nature of the alkenes influences the stereoselectivity to the extent that e.e values seem to obey a linear free energy relationship with Hammett constants [9], [11].

As far as the hydroborating reagent is concerned, the catecholborane seems to be the borane source that has the most favourable effect on the experimental hydroboration reactions, although it is not yet clear exactly why. The following factors, however, may help to explain its performance. The fact that catecholborane is monomeric and coplanar means that it is spatially undemanding; therefore its addition to the metal is without hindrance. Also, the electronic nature of this borane is unusual. The five-ring heterocycle is aromatic and has a significant B-O double bond character, but B-H also shows a pronounced enhanced acidity. On the other hand, the principal problem is the disproportion to BH_3 and the catechol-bridged boronate ester $B_2(C_6H_4O_2)_3$ (**35**) [12].

Several fundamental questions about the source of chirality are largely unsolved: for example, how is chirality transferred to the reactive site and how much chirality is involved? Recently, Zhang et al. reported that the dihedral angles of chiral biaryl ligands influence the enantioselectivity of the asymmetric hydrogenation reaction [13]. Harada et al. found that there was a parabolic relationship between the e.e and the torsion angle of the two-biaryl moieties in the asymmetric Diels-Alder reaction of acrylates with cyclopentadiene using homotopic biaryldiol ligands [14]. In addition, Lipkowitz and col. were able to reproduce exactly the same e.e trend as the one observed by Harada through a measure of chirality content because of continuous

chirality metrics (CCM) [15], [16]. They introduced the idea of chiraphore, which is the part of the molecule responsible for stereoinduction. In fact, they established that a stereoselective catalyst is efficient when its maximum capacity to differentiate between two enantiomers occurs in the reaction site, where the substrate/catalyst interactions are able to discriminate between the reaction pathways leading to one enantiomer or the other.

The nature of the catalytic cycle of the alkene hydroboration using the Wilkinson catalyst $RhCl(PPh_3)_3$ was first reported by Männig and Nöth in 1985 [17], and has been addressed experimentally [18], by means of quantum chemistry methods [19]. It was reviewed recently [20] (Figure 2). They proposed that the catalysed reaction might proceed via oxidative addition of borane to the rhodium (I) centre followed by alkene coordination. Whether the following pathway could be alkene insertion into Rh-H or Rh-B is still controversial, however. In general, all authors seem to agree that the last sequence could be the reductive elimination of the arylboronate ester. Of all the steps considered in this catalytic cycle, the coordination of the alkene to the metal center could be the one controlling the regio- and enantioselectivity.

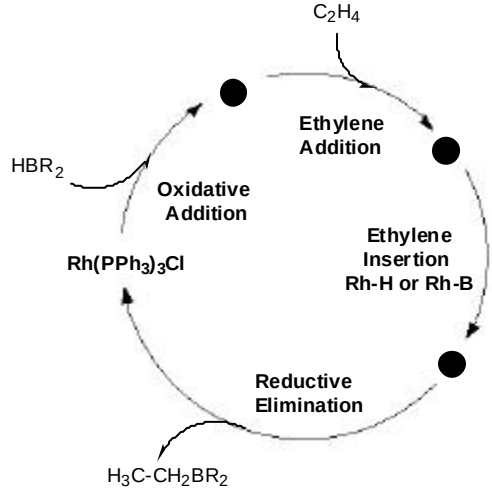


Figure 2

The combination of several techniques, (X-ray crystallography, kinetics and NMR) has enabled to draw a detailed picture of the reaction mechanism of asymmetric hydrogenation. This was partly made possible by the relative stability of some intermediates in the catalytic cycle, such as the key hydridealkylrhodium intermediate.

To the best of our knowledge, only few attempts have been made to characterise intermediates in the hydroboration reaction. These intermediates make it possible for their activity and selectivity to be rationalised. It appears that the true catalytic species are quite transient, at least when catecholborane is used as the hydroborating reagent. Brown et al. [21] proposed as a plausible intermediate a penta-coordinated complex H-Rh/Quinap/catecholborane/vinylarene based on X-ray structural data on the $PdCl_2$(Quinap) complex combined with Chem 3D structures of the borane and alkene. This model assumed that the hydride was in an axial position and coplanar with a coordinated C=C substrate, (Figure 3).

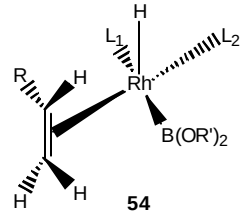


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Figure 3

In addition, this model suggested that the influence of electronic effects on the enantiomeric excess might arise from the potential π-stack formed between the aryl group of the substrate and a nearby P-aryl group of the ligand. Also recently, Chan et al. [11] have suggested that transition-state models, on the basis of the penta-coordinated Rh/H/Pyphos/catecholborane/vinylarene complexes, can explain the electronic effect of modified substrates and/or ligands in asymmetric hydroboration. The latter work, proposed that vinylarenes with electron-releasing substituents coordinate more strongly to the rhodium center than the vinylarenes with electron-withdrawing substituents. The authors speculated that electron-rich substrates may be

closer to the metal than their electron-poor analogues, thus improving stereochemical communication and providing higher enantioselectivity. Although, it is true that interactions between the substrates and the rhodium-ligand-catecholborane complex play an important role, their real nature is still unknown.

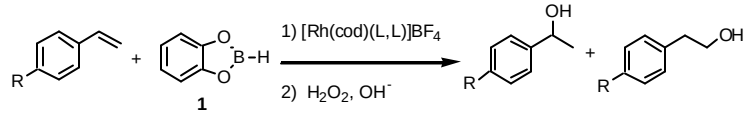
Finally it should be pointed out that the role of the ligand, the substrate and the hydroborating reagent need to be understood, if ligand design is to be free from trial and error approaches and the catalytic system is to perform more predictably after small variations in the reactants and catalysts. This chapter aims to provide more information about these influences and the intermediates involved in the asymmetric catalytic cycle.

2. Results and discussion

2.1. Role of the ligand

We made a comprehensive study of (R)-Binap and (R)-Quinap as ligands, to determine how they affect the hydroboration/oxidation of several electronically different vinylarenes. While the Binap is a homotopic atropoisomeric P,P ligand which chelates with the metal to form a seven-member ring, the heterotopic atropoisomeric P,N Quinap shares a six-member ring with the metal center. Comparing Quinap to its parent ligand Binap, the P,N ligand is less bulky in the region of the isoquinoline because it replaces one of the diphenylphosphinonapthalene moieties. This structural difference, in conjunction with the electronic features of the P,N ligand, may explain why the enantioselectivity in the hydroboration/oxidation of vinylarenes dramatically increases when Quinap is the modifying ligand of Rh(I), (Table 1). P,N ligands that are structurally very similar to Quinap, also behave in a similar way, [7], [8e], [9-10], [22]. The reaction with Binap requires low temperatures for a satisfactory e.e [8a].

Table 1. Influence of the ligand ((L,L)= (R)-Binap, (R)-Quinap) on the asymmetric hydroboration/oxidation of vinylarenes with cationic rhodium complexes.[a]



Conversion > 90%

Entry	Catalytic System	R	Branched	e.e [b] (%)
1	[Rh(cod)(R)-Binap]BF_4	H	99	57
2	[Rh(cod)(R)-Quinap]BF_4	H	95	88
3	[Rh(cod)(R)-Binap]BF_4	Me	99	58
4	[Rh(cod)(R)-Quinap]BF_4	Me	97	89
5	[Rh(cod)(R)-Binap]BF_4	F	99	57
6	[Rh(cod)(R)-Quinap]BF_4	F	96	80

[a] Standard conditions: substrate/borane/Rh complex = 1/1.1/0.01. Solvent: THF. T: 25^0C. Time: 1h. [b] (R) Configuration determined by GC with chiral column FS-Cyclodex β-IP, 50m x 0.25mm.

In order to study the specific effects of the ligands on the catalytic hydroboration of electronically different vinylarenes, a model must be established for the rhodium intermediate that is responsible for the diastereoselection. Several theoretical studies into the catalysed olefin hydroboration reaction have used model ligands, (i.e. PH_3, and model hydroboration reagents, H-$B(OH)_2$ [19-20]), and dealt with whether the mechanism is *associative* or *dissociative* with regards to phosphine, and whether alkene is inserted through hydride or boryl migration. However, several studies agree that the first step in the catalytic cycle is the oxidative addition of H-$B(OR)_2$ to the Rh centre in $RhCl(PPh_3)_3$, yielding a penta-coordinated hydroboryl complex such as [$RhL_2HCl(B(OR)_2)$], where L=PH_3, PMe_3, P^iPr_3, PPh_3, (Figure 4), [17-18], [23].

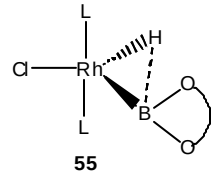


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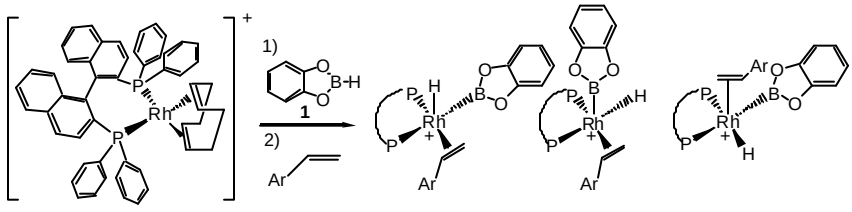
Figure 4

Very few of the metal-boryl complexes isolated from the oxidative addition of H-B(OR)$_2$ to metal complexes [24], have involved rhodium complexes [25]. In addition, there are serious difficulties in isolating rhodium intermediate species during the fast hydroboration reaction, where the chiral ligand, the hydride, the boryl and the olefin are coordinated to the metal. All these events have limited the determination of reaction intermediates in comparison with other metal complexes [26].

In an attempt to clarify the nature of the key intermediates in the hydroboration reaction, we performed a multinuclear NMR spectroscopic study of styrene and catecholborane addition to the catalyst precursor [Rh(cod)(L,L)]BF$_4$, where (L,L)= (R)-Binap and (R)-Quinap. When the ligand is Binap, several different isomers were formed from the stoichiometric addition of catecholborane and styrene to the [Rh(cod)(R)-Binap]BF$_4$ complex, (Scheme 1).



56 **57** **58** **59**

Scheme 1

Initially, the ^{1}H NMR spectra of free catecholborane carried out in CD_3CN showed a quadruplet centred at 4.25ppm ($J_{H\text{-}B}$=197.2Hz), due to the H bonded to B (spin 3/2, 80.4%, natural abundance, spin 3, 19.6%, natural abundance). After the borane reagent and styrene had been added to complex **56**, the resonances of the hydride ligand appeared as an upfield shift centred at δ=-14.51ppm as a double doublet of doublets, (Figure 5(a)). The three coupling constants, $J_{H\text{-}Rh}$=18Hz, $J_{H\text{-}P}$=14Hz, $J_{H\text{-}P}$= 9Hz, are indicative of the hydride position *cis* to two non-equivalent phosphorous nuclei. It is known that the hydride located *trans* to phosphorous is associated with higher coupling constant values ($J_{H\text{-}P(trans)}$=110-130Hz). A selective ^{31}P decoupling experiment significantly simplified the hydride signal in the ^{1}H NMR, which

showed a broad doublet centred at the same chemical shift δ=-14.51 ppm. The inequivalence of the phosphorous nuclei may be because one P is *trans* to the catecholboryl, while the other is *trans* to the styrene. The experiment suggests to us the plausible formation of isomer **57**, (Scheme 1). The ^{11}B and the ^{31}P NMR spectra confirm this arrangement. The initial doublet due to the B bonded to H in free catecholborane, (δ=28.88ppm, J_{H-B}=197.2Hz), was shifted upfield as a broad resonance (δ=21.40ppm) after catecholborane and styrene were added to the metal complex. $^{31}P\{^{1}H\}$ NMR spectra in d^{8}-THF, also showed a significant shift from the initial doublet centred at δ=26.15ppm (J_{P-Rh}=145.5Hz), in the [Rh(cod)(R)-Binap]BF_4 complex, to two new doublets centred at δ=46.93ppm (J_{P-Rh}=207.8Hz) and δ=46.70ppm (J_{P-Rh}=207.8Hz) (Figure 5(b)). Similar resonances have been observed in the literature by monitoring ^{1}H NMR and ^{31}P NMR spectroscopy after catecholborane oxidative addition reaction on [IrX(CO)(P,P)], (where (P,P)= dppe, chiraphos), [27].

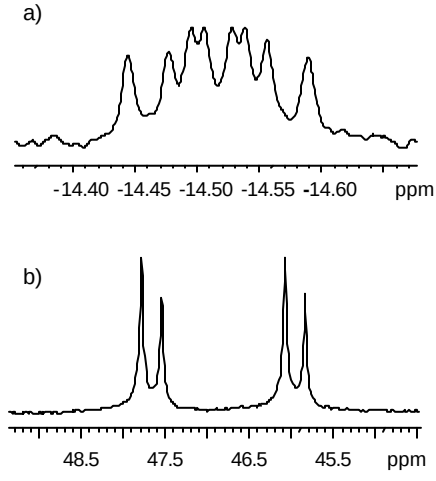
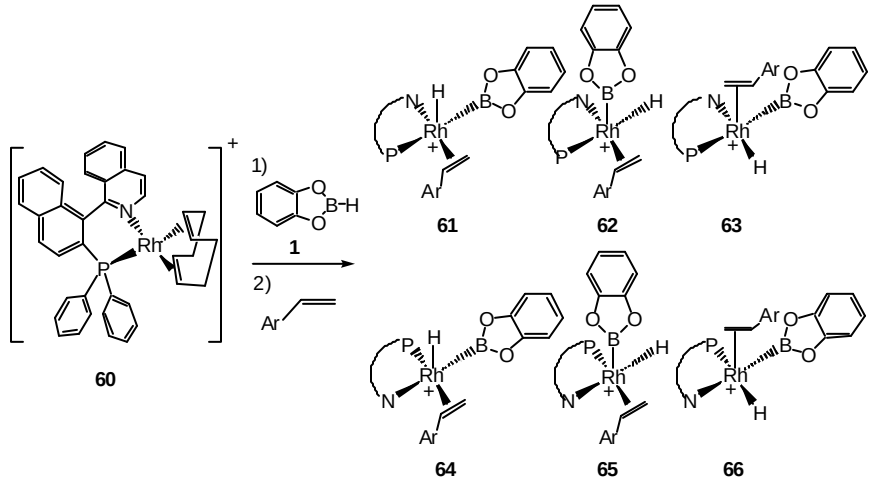


Figure 5.

New NMR signals appeared after catechol-borane and styrene had been added to complex **56** (a) hydride signal in ^{1}H NMR; (b) ^{31}P NMR.

Styrene coordination to rhodium was confirmed by the upfield shift of the alkene hydrogen signals from δ=5.22, 5.73ppm in free styrene to δ=4.82, 5.43ppm in the rhodium isomer formed.

What is more, the *cis* addition of catecholborane and styrene to [Rh(cod)(R)-Quinap]BF_4, may involve the formation of a larger number of isomers, (Scheme 2). We tried to monitor the ^{1}H, ^{11}B and ^{31}P NMR spectra of the *cis* addition of catecholborane and styrene on the [Rh(cod)(R)-Quinap]BF_4 complex, but no hydride signals appeared upfielded in the ^{1}H NMR spectra. The most significant features observed were, first, the slight shift in the initial doublet in the ^{31}P NMR, from δ=32.67ppm, ($J_{P\text{-}Rh}$=140.8Hz) in [Rh(cod)(R)-Quinap]BF_4, upfielded to δ=32.25ppm, ($J_{P\text{-}Rh}$=140.7Hz); and second, the displacement of both signals due to H and B nuclei from free catecholborane, which indicates that the borane reagent was no longer free. We suggest on the basis of literature precedent [24a], [28-29] that, alternatively, a three-centre bonding interaction between Rh-B-H might have taken place. Although we could not demonstrate that a particular isomer was formed after the *cis* addition of catecholborane and styrene to [Rh(cod)(R)-Quinap]BF_4, we assumed that the key intermediate could be any of the isomers shown in Scheme 2, by analogy with the Rh-Binap analogue catalytic system. Brown [9] and Chang [11] suggested that the key intermediate in this case, would probably be **61**.



Scheme 2

One must consider at this point the nature of the stereodefining step in the catalytic cycle. Brown et al. [9], proposed that the coordination step of the alkene to rhodium is not necessarily the stereodefining event but that the insertion step could be. Indeed, Rh-C bond formation is one of the most electronically and sterically demanding steps in the catalytic cycle, but unfortunately the insertion of the alkene through boryl and hydride migration is still not clear. Arguments in favour of boryl migration are given by Ziegler et al. [18c], [19a, c], although the new C-B coupling could provide undesired by products. In contrast, Evans et al. [18a, b], [19b], [30], suggest that hydride insertion is preferred and even favoured if sterically demanding electron-withdrawing ligands are used. In this context, we believe that the insertion step is not the key determining step for regio- and enantioselectivity. The stereochemistry of the final product is probably determined in a previous step such as the one in which the olefin coordinates to the metal and generates intermediates **61** and **57**. The complete picture for the asymmetric induction could involve the consecutive sequences for the alkene like coordination + insertion. For instance, a non prochiral alkene such as acenaphthene reacts enantioselectively (e.e = 86% with [Rh(cod)(S)-Quinap]BF_4, [9]) as a result of the different chemical environment in its approach to the metal center, (Figure 6).

As part of a joint project, the parallel studies made by Bo and Daura, using DFT calculations and QM/MM strategies, were in excellent agreement with the trend of our experimental results [1]. These calculations allow us to study the origin of regio- and stereoselectivity in the rhodium-catalyzed hydroboration reaction of vinylarenes, and the role of the steric and/or electronic features of the ligand. Although this theoretical study does not come within the scope of this thesis, their results complement our own experimental studies. Therefore, some of their most important results are also included in the present discussion.

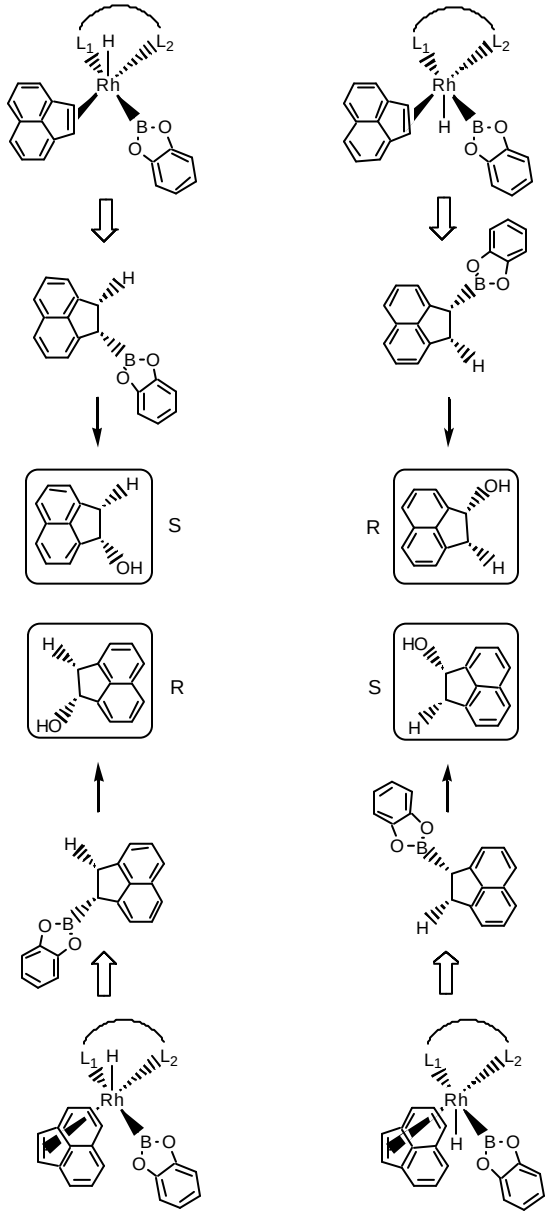


Figure 6

Bo and Daura assumed that the relative stability of the possible isomers was directly related to their population and, therefore, the most stable isomers were those that determined the reaction outcome. At this point, it should be pointed out that the isomers were distinguished by the different interactions between the substrate and the catalyst. The most stable isomer, then, should determine the reaction outcome, thus demonstrating that the coordination of the alkene to the metal center is the stereodefining step. On the basis of our experimental results from the NMR data, the computational modelling study was focused on the squared-pyramid based intermediates type **61** ((L,L) = Quinap) and **57** ((L,L)= Binap), where the hydrido ligand was located up side (Figure 7, Group A) or down side (Figure 7, Group B).

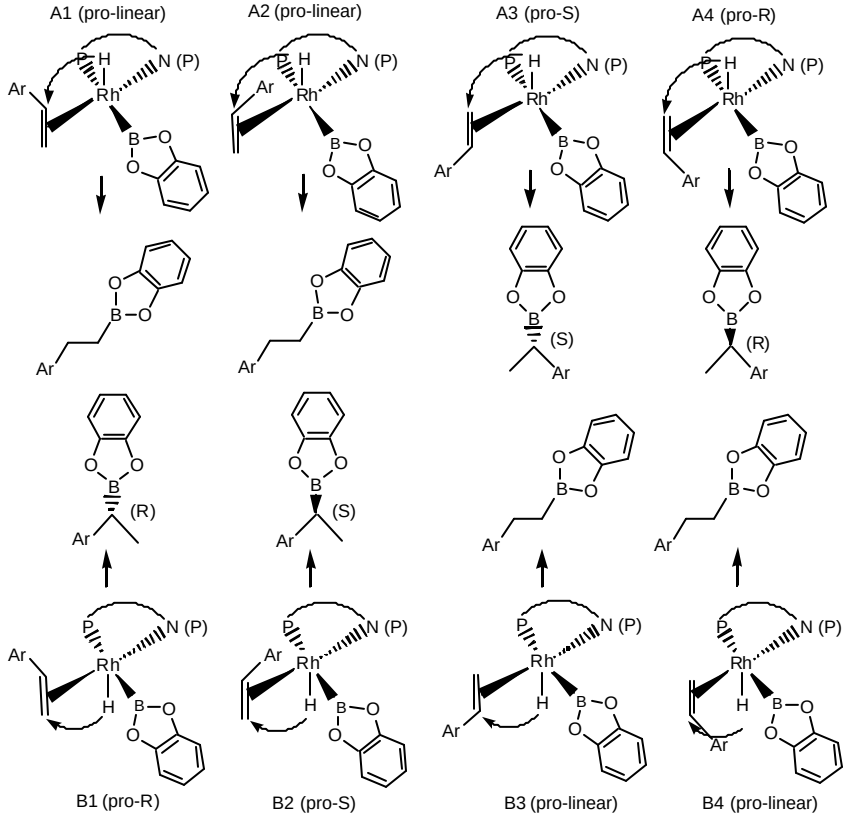


Figure 7

From all the eight isomers associated with the relative coordination of the alkene in relation to the Rh-hydride complex, pro-linear intermediates appeared at relative energy values that were higher than those of pro-branched intermediates, favouring the expected branched products. As far as the enantioselectivity is concerned, when (L,L)= Quinap and the alkene= styrene, the pro-R (B1) and pro-S (B2) isomers were the two most stable forms, with an energy difference of 4.1 kcal.mol^{-1}. However, when (L,L)= Binap, the second most stable isomer after the pro-R (B1) intermediate was found to be the pro-S (A3) with an energy difference of 0.3 kcal.mol^{-1}.

Such a small difference in energy has been shown by Bo and Daura to explain the lower stereodifferentiation of the P,P ligand. In addition, an analysis of the intermolecular interactions revealed that intermolecular π-π stacking interactions between the substrate and the ligand, the substrate and the hydroborating reagent, and the hydroborating reagent and the ligand, could be the reason for the relative stability of the key intermediates.

These theoretical predictions agree with the catalytic experimental data, and also with some of the data reported in the literature where stereodifferentiation becomes temperature dependent in related chiral P,N ligands, [1b]. This is the case for rhodium complexes modified with the atropoisomeric ligand Pyphos (**31**) [11], (2-(2'-diphenylphosphino-4',6'-di-*tert*-butyl-1'-phenyl)-3-methyl-pyridine), which requires temperatures around 0 ^{0}C to provide enantiomeric excess values comparable to the Rh-Quinap in the hydroboration/oxidation of vinylarenes, (Figure 8).

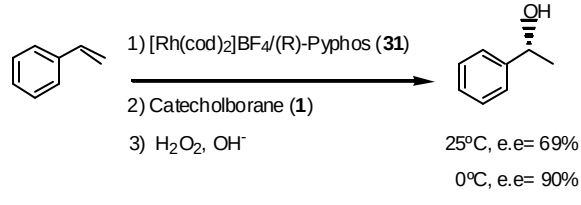
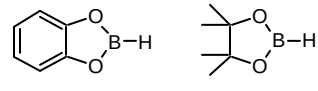


Figure 8

2.2. The role of the hydroborating reagent

The oxidative addition of the hydroborating reagent is considered to be one of the first steps in the catalytic cycle of the hydroboration reaction. Two events are essential to the success of this step: a basic ligand must modify the catalytic system, and the hydroborating reagent must have a boron atom that is sufficiently Lewis-acidic to be catalytically activated for the B-H addition. If we focus on the reagent, diorganyloxyboranes H-B(RO)$_2$ and in particular those which are cyclic compounds show an extremely high degree of Lewis acidity, [31]. In this context, catecholborane (**1**) (Figure 9), is one of the most commonly used, probably because it facilitates B-H addition to the metal and the boryl coordinated to the metal has a favourable steric profile. Although, catecholborane has proved to be the most versatile diorganyloxyborane so far, it is still far from ideal, because its intrinsic instability and degradation give rise to complex mixtures of highly active species that are responsible for a number of side reactions during the catalytic reaction, (for example alkene isomerisation, hydrogenation, vinylboronate ester formation [32] and BH_3 addition [12]). To avoid those difficulties, it is recommended to redistill catecholborane just before it is used and, for slow reactions to use solvents that are not sensitive to Lewis acids as toluene instead of tetrahydrofurane. Therefore, alternative hydroborating reagents have to be considered although very few have been isolated. The pinacolborane (**5**), (Figure 9), is another diorganyloxyborane with a five-member ring, but unlike catecholboronate, it is stable and insensitive to moisture. The pinacolborane has been qualitatively tested in the reactivity of transition metal-catalysed hydroboration of alkenes, [12], [33], although to the best of our knowledge its influence on the selectivity has not been reported yet.



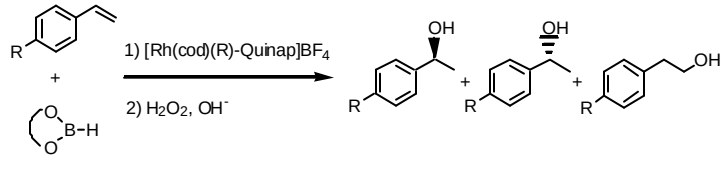
1 **5**

Figure 9

In the present study, we have expanded the scope of the asymmetric hydroboration/oxidation reaction of vinylarenes with pinacolborane as hydroborating reagent.

In general, we found that [Rh(cod)(R)-Quinap]BF_4 as precursor of catalyst, provided slightly higher percentages of the enantioselective branched product when catecholborane is used as hydroborating reagent instead of pinacolborane, (Table 2, entries 1 and 2). This trend is also observed for hydroboration/oxidation of substituted styrenes, such as electron-rich styrenes (Table 2, entries 3 and 4) but not so much for electron poor-styrenes (Table 2, entries 5 and 6).

Table 2. Asymmetric hydroboration/oxidation of vinylarenes towards (R)-(+)-*sec*-alcohol catalysed by [Rh(cod)(R)-Quinap]BF_4 complex and catechol-borane (**1**) or pinacolborane (**5**) as hydroboration reagent.[a]



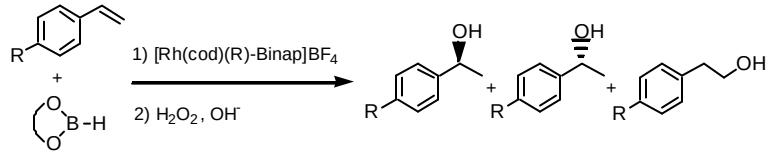
Entry	Borane	R	Yield (%)	Branched (%)	e.e [b] (%)
1	Catecholborane	H	99	95	88
2	Pinacolborane	H	99	75.5	73
3	Catecholborane	Me	98	97	89
4	Pinacolborane	Me	93	91.5	86
5	Catecholborane	F	97	96	80
6	Pinacolborane	F	93	93	83

[a] Standard conditions: substrate/borane/Rh complex = 1/1.1/0.01. Solvent: THF. T: 25^{0}C. Time: 1h. [b] (R) Configuration determined by GC with chiral column FS-Cyclodex β-IP, 50m x 0.25mm.

When the chiral auxiliary ligand (R)-Binap modified the rhodium complex, the differences in the catalytic activity were notable, starting from the fact that the reactivity

was lower than for [Rh(cod)(R)-Quinap]BF_4. Our preliminary experiments indicated that the hydroboration/oxidation of styrene with pinacolborane provided similar percentages of the primary and the secondary alcohol. Furthermore, we observed a change in the absolute configuration of the branched alcohol when catecholborane was replaced by pinacolborane, which also indicated significant structural differences in the enantioselective step of the catalytic cycle, (Table 3, entries 1 and 2).

Table 3. Asymmetric hydroboration/oxidation of vinylarenes towards *sec*-alcohol catalysed by [Rh(cod)(R)-Binap]BF_4 complex and catecholborane (**1**) or pinacolborane (**5**) as hydroboration reagent.[a]



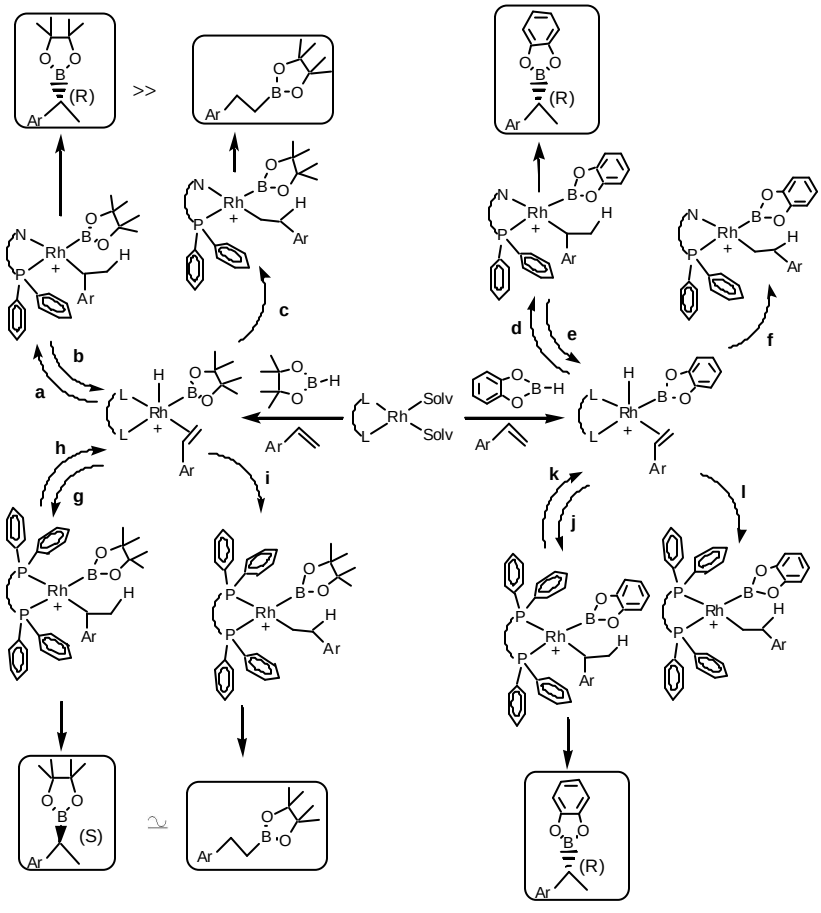
Entry	Borane	R	Yield (%)	Branched (%)	e.e [b] (%)
1	Catecholborane	H	92	99	57(R)
2	Pinacolborane	H	97	50	18(S)
3	Catecholborane	Me	87	99	58(R)
4	Pinacolborane	Me	54	41	16(S)
5	Catecholborane	F	91	99	57(R)
6	Pinacolborane	F	46	46	16(S)
7	Catecholborane	MeO	89	99	60(R)
8	Pinacolborane	MeO	46	58	38(S)
9[c]	Catecholborane	MeO	77	99	70(R)
10[d]	Catecholborane	MeO	25	99	77(R)
11	Catecholborane	Cl	93	99	65(R)
12	Pinacolborane	Cl	71	45	4(S)

[a] Standard conditions: substrate/borane/Rh complex = 1/1.1/0.01. Solvent: THF. T: 25^0C. Time: 1h; [b] Configuration determined by GC with chiral column FS-Cyclodex β-IP, 50m x 0.25mm; [c] Temperature: 0^0C; [d] Temperature: -78^0C.

Because of these results, we explored the catalytic hydroboration/oxidation reaction of substituted styrenes, and we also observed attenuated regioselectivity and reversed enantioselectivity, (Table 3). Significant changes were observed for the corresponding *p*-MeO-styrene: e.e values were around 60% for the (R)-(+)-*sec*-alcohol with catecholborane and 38% for the (S)-(-)-*sec*-alcohol with pinacolborane, (Table 3, entries 7 and 8). The variation in the configuration is even more pronounced at low temperatures, where a more forced metal-complex is expected, (Table 3, entries 9 and 10).

In order to rationalise the influence of the hydroborating reagent on both reactivity and selectivity, we will again take into account the catalytic cycle. After the oxidative addition and alkene coordination steps, the rhodium intermediate complex accommodates both the hydroborating reagent and the alkene itself. One of the most striking differences between both reagents, the catecholborane (**1**) and the pinacolborane (**5**), is that the steric demand of the pinacolborane is higher. It seems that the more crowded environment around the rhodium center carries the lower reactivity and selectivity towards the secondary alcohol, (Scheme 3). The fact that the isoquinoline region of Quinap was more tolerant to the accommodation of pinacolborane meant that the catalytic activity was similar to when catecholborane was used, although small quantities of the primary alcohol were also formed. The favoured η^3-coordination of vinylarenes with the Rh/(R)-Quinap/pinacolborane intermediate, allowed mainly the migratory insertion towards the secondary-alkyl rhodium complex, which eventually provided the Markovnikov alcohol product via reductive elimination, (Scheme 3, path a). The primary insertion observed when pinacolborane is involved could be due to a β-H elimination, (Scheme 3, path b), followed by a primary reinsertion sequence, (Scheme 3, path c). On other hand, when catecholborane is the borane reagent in the Rh/(R)-Quinap intermediate, the almost exclusive formation of the secondary-alkyl complex may proceed at a faster rate than that of β-H elimination (Scheme 3, paths d and e). Analogous behaviour is observed with the use of catecholborane and Rh-(R)-Binap complex, (Scheme 3, path j, k, l). In the reaction of Rh-(R)-Binap and pinacolborane, vinylarenes presumably undergo a more facile β-H elimination (Scheme 3, path h), due to the very sterically congested secondary-alkylrhodium complex following a primary reinsertion sequence, (Scheme 3, path i).

However, we can not rule out the possibility of a direct initial primary insertion of the alkene because of the steric hindrance of the Rh/(R)-Binap/pinacolborane intermediate, followed by reductive elimination, which provides the primary product in competition with the favoured secondary boronate ester. The moderate reactivity of Rh-(R)-Binap/ /pinacolborane with substituted styrenes would be in agreement with this latter assumption.



Scheme 3

Plausible catalytic pathways: oxidative addition of the hydroborating reagent to the rhodium complex followed by the migratory insertion of the alkene into the M-H bond (the migratory insertion of the alkene into the M-B bond could also be considered) and reductive elimination of the alkylboronate esters.

As far as the enantioselectivity is concerned and taking into account the experimental data, the reversal in enantioselectivity between Rh/(R)-Quinap/ /pinacolborane and Rh/(R)-Binap/pinacolborane has to be highlighted. Therefore, the data must be analysed further if the influence of these hydroborating reagents on the asymmetric induction is to be understood.

Again, Bo's and Daura's parallel studies with DFT calculations and QM/MM strategies were in excellent agreement with the trend of our experimental results [1b]. As that used in the previous theoretical studies all eight possible isomers (Figure 7, A1-A4, B1-B4) were considered in the search for the most stable isomer of the metal complexes Rh/ligand/borane/styrene, (where the ligand was (R)-Quinap and (R)-Binap, and the borane was catecholborane and pinacolborane). Figure 10 shows the relative stability of the most stable isomeric forms in agreement with the experimental data, and it shows the following:

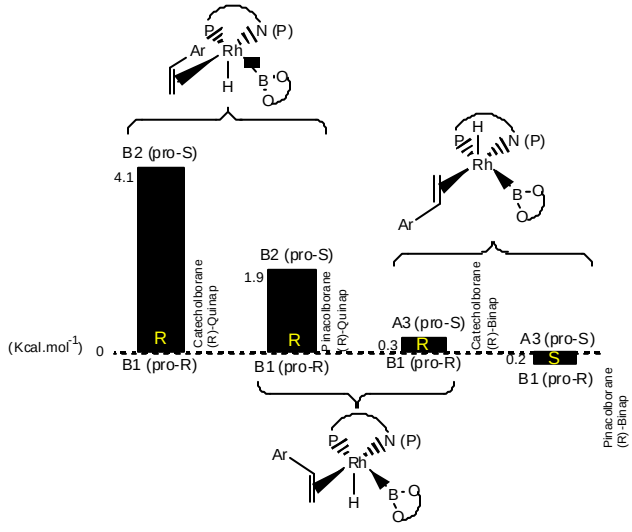


Figure 10

a) The difference between isomer B1 (pro-R) and B2 (pro-S) decreased from 4.1 to 1.9 when catecholborane was substituted with pinacolborane. This may explain the decrease in the enantiomeric excess observed with this hydroboration reagent exchange, in the hydroboration of styrene catalysed by Rh/(R)-Quinap.

b) For the Rh/(R)-Binap/styrene catalytic systems, the most stable isomer was B1 (pro R) when catecholborane was the hydroborating reagent and A3 (pro-S) when it was pinacolborane. These differences in the most stable isomer, may explain the reverse enantioselectivity observed. The low energy values between the first and the second most stable isomer, also agree with the low asymmetric induction obtained with Rh/(R)-Binap/borane catalytic systems.

Bo and Daura explained the different stabilisations of the isomers by the different π- π stacking interactions between the ligand, the hydroborating reagent and the substrate, [1].

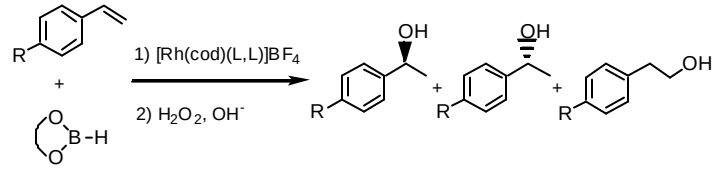
2.3. The role of the substrate

To complete the overall picture of the factors controlling the hydroboration reaction, we examined the reactivity of several other substituted vinylarenes to elucidate the role of substituents on the overall product distribution.

The enantioselectivity observed in the hydroboration/oxidation of substituted styrenes depends significantly on the aryl ring substituents. Brown et al., suggested a simple trend related to the inductive electronic effect of the substituents [9], for the rhodium catalyst complex modified with Quinap and other similar ligands and with catecholborane as the hydroborating reagent. For electron-releasing *para*-substituents, such as methyl, (Table 4, entry 1), enantiodifferentiation is higher than for the electron-withdrawing *para*-substituents, such as fluoride, (Table 4, entry 3). Therefore the enantiomeric excess increased as the electron-releasing character of substituents in styrene increased: *p*-F-styrene < styrene < *p*-Me-styrene.

On the basis of Brown's observation and in order to prove a general tendency associated to the electronic properties of the substrate, we analyzed the electronic effects induced by the *para* substituents of styrene on the Rh/ligand/borane intermediates, (where the ligand was (R)-Binap (**25**) and (R)-Quinap (**28**), and the borane was catecholborane (**1**) and pinacolborane (**5**)), (Table 4).

Table 4. Asymmetric hydroboration/oxidation of substituted vinylarenes towards *sec*-alcohol catalysed by $[Rh(cod)(L,L)]BF_4$ ((L,L)= (R)-Binap (**25**) and (R)-Quinap (**28**)) and catecholborane (**1**) or pinacolborane (**5**) as the hydroboration reagent.[a]



Entry	R	(L,L)	Borane	e.e [b] (%)
1	Me	(R)-Quinap	Catecholborane	89 (R)
2	H	(R)-Quinap	Catecholborane	88 (R)
3	F	(R)-Quinap	Catecholborane	80 (R)
4	Me	(R)-Quinap	Pinacolborane	86 (R)
5	H	(R)-Quinap	Pinacolborane	73 (R)
6	F	(R)-Quinap	Pinacolborane	83 (R)
7	Me	(R)-Binap	Catecholborane	58 (R)
8	H	(R)-Binap	Catecholborane	57 (R)
9	F	(R)-Binap	Catecholborane	57 (R)
10	Me	(R)-Binap	Pinacolborane	16 (S)
11	H	(R)-Binap	Pinacolborane	18 (S)
12	F	(R)-Binap	Pinacolborane	16 (S)

[a] Standard conditions: substrate/borane/Rh complex = 1/1.1/0.01. Solvent: THF. T: 25^0C. Time: 1h. [b] Configuration determined by GC with chiral column FS-Cyclodex β-IP, 50m x 0.25mm.

A slight tendency in favour of higher asymmetric induction for electron-rich vinylarenes was observed irrespectively of whether catecholborane (Table 4, entries 1-

3) or pinacolborane (Table 4, entries 4-6) was added to [Rh(cod)(R)-Quinap]BF_4. However, at room temperature, the hydroboration carried out with [Rh(cod)(R)-Binap]BF_4 showed no trend when both hydroborating reagents were used. This might be because the Rh-(R)-Quinap complex favours π-π interactions between the more electronically-rich substrates and the ligand or catecholborane/pinacolborane reagent. However, when Rh-(R)-Binap complex is involved in any of these π-π interactions, the differentiation between the isomers of the key rhodium intermediates seems to diminish.

Bo and Daura undertook a deeper analysis [1], to reveal that the difference between the two most stable isomers B1 (pro-R) and B2 (pro-S), increased as the electron-withdrawing character of the styrene substituents decreased, (Figure 11.a).

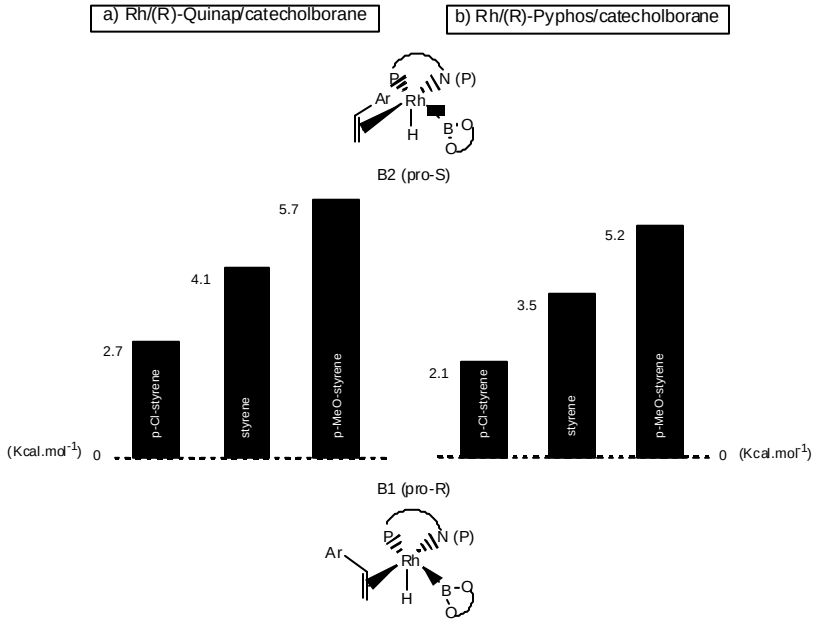


Figure 11

Like the enantiodifferentiation observed in the experimental data, the difference in the relative stability between B1 and B2 also seems to have a clear electronic origin and is therefore related to the nature and strength of the intermolecular π-π interactions observed in the key rhodium intermediates.

Bo and Daura also demonstrated [1] that enantiodifferentiation towards electronically different vinylarenes, may already be present in the rhodium key intermediates, in the hydroboration reaction with the catalytic system Rh-(R)-Pyphos [11]. Thus, the more enantioselective hydroboration/oxidation on the branched alcohol from *p*-Cl-styrene (e.e= 79%), styrene (e.e= 90%) to *p*-MeO-styrene (e.e= 94%), the higher increment in energies between B1 and B2, (Figure 11.b). However, the relative energy values in this series are lower than those for the Rh-(R)-Quinap catalytic system, which should also explain the temperature dependence (0^0C required) in the case of Rh-(R)-Pyphos [11].

2.4. The role of the metal

The catalytic hydroboration reaction is not limited to rhodium complexes [34]. However, the successful enantioselective transformation of vinylarenes, and to a lesser extent of norbornene, has long been restricted to the use of the cationic and neutral complexes of this particular transition metal. Recently, Bonin and Micouin et al. [35] reported an example of the complete reversal of enantioselectivity between Rh and Ir systems in the hydroboration reaction of *meso* hydrazine substrates. This made us wonder when the Ir-Binap catalytic system is also a suitable catalyst for the hydroboration of vinylarenes.

When complex [Ir(cod)(R)-Binap]BF_4 was used under the same hydroboration/oxidation reaction conditions as the analogous rhodium system, (substrate/catecholborane/Ir complex = 1/1.1/0.01, in THF, 25^0C, 1h), conversion was complete but regioselectivity was only about 30% for 1-phenylethanol. The most surprising fact is that enantioselectivity was, under those conditions, almost nil. The Ir/(R)-Binap complex did not seem to induce asymmetry at all and, in addition, there was also a dramatic decrease in the regioselectivity in favour of the linear product, due to the metal exchange.

On trying to rationalise the reversal of regioselectivity shown by the iridium complexes, we came back to the central question of whether the insertion step in the catalytic cycle takes place by hydride migration or boryl migration. In fact, experimental [36] and theoretical studies [29a] have proposed two main catalytic cycles: one of them involves a migratory insertion into the metal-H bond [18a, b], [19b], [30], and the other favours the migration of a boryl group [18c], [19b]. It has also been observed that these two pathways should lead to opposite regioisomers or, in the case of *meso* substrates, enantiomers. It has been postulated [35], that iridium catalysed hydroboration involves the Ir-B migratory insertion step while the rhodium catalysed hydroboration involves the Rh-H migratory insertion, (Figure 12). Those different mechanistic pathways could explain the opposite regioselectivity observed between Ir-Binap and Rh-Binap catalytic systems for our experimental hydroboration reaction.

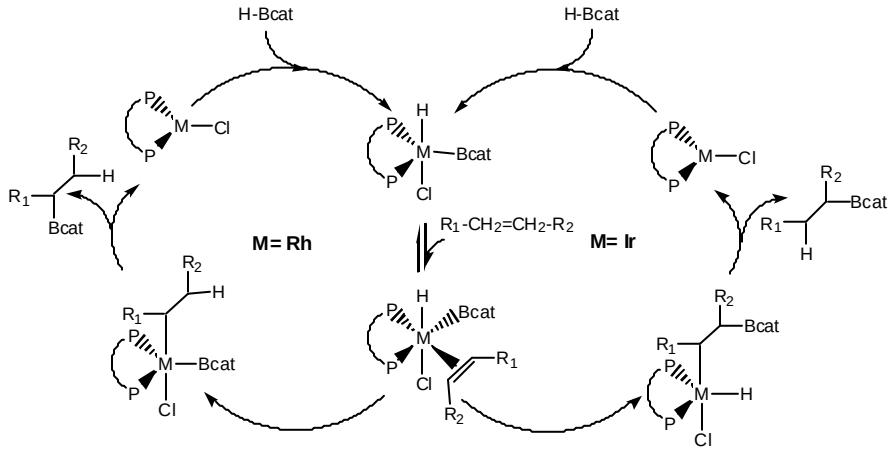


Figure 12

In order to establish why the enantioselectivity is so affected by the change in the metal of the catalytic system, Bo and Daura calculated that the relative stability of the B1 (pro-R) isomer and B2 (pro-S) isomer in both rhodium and iridium key intermediates were significantly different (Figure 13). Again, the nature of the π-π-

stacking interactions provides extra-stabilisation for the B2 isomer in Ir/(L,L) catalytic systems.

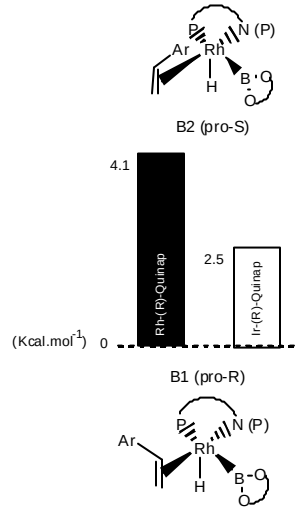


Figure 13

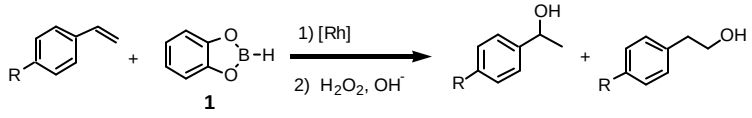
2.5. The influence of the electronic nature of the catalytic system

In view of the fact that both the regio- and the enantioselectivity of the hydroboration of vinylarenes depend heavily on the structural features of the catalysts applied, we felt that it could be interesting to focus on the electronic nature of the rhodium (I) source with a coordinated and non-coordinated counterion.

We made a comparative study of the asymmetric hydroboration of vinylarenes with [Rh(cod)(R)-Quinap]BF_4 and [Rh(μ-Cl)(cod)]$_2$/2eq.(R)-Quinap complexes, (Table 5). Like the cationic catalysts, we noticed a preferential secondary insertion of the styrene into the neutral rhodium complex formed from [Rh(μ-Cl)(cod)]$_2$/2eq.(R)-Quinap. However, the neutral catalytic system seems to have some additional influence and favours the enantioselectivity at values up to 94% for (R)-(+)-1-phenylethanol, (Table 5, entries 1 and 2). Electronically different vinylarenes were selected to study the scope of the neutral catalytic systems. In all cases, for styrenes

with electron-withdrawing and electron-releasing substituents, the neutral catalytic system increased enantioselectivity to values between 91.5% (*p*-F-styrene) and 96% (*p*-MeO-styrene), (Table 5, entries 3-6).

Table 5. Asymmetric hydroboration/oxidation of vinylarenes with catecholborane, towards (R)-sec-alcohol, catalysed by cationic and neutral rhodium complexes [a]



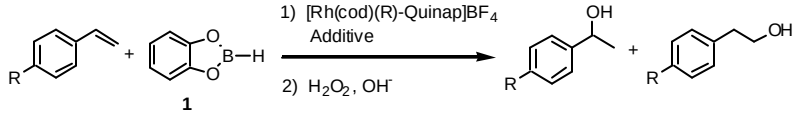
Entry	Catalytic System	R	Yield (%)	Branched (%)	e.e [b] (%)
1	[Rh(cod)(R)-Quinap]BF_4	H	92	95	88
2	[Rh(μ-Cl)(cod)]$_2$/(R)-Quinap	H	99	98	94
3	[Rh(cod)(R)-Quinap]BF_4	MeO	98	96	94
4	[Rh(μ-Cl)(cod)]$_2$/(R)-Quinap	MeO	92	99	96
5	[Rh(cod)(R)-Quinap]BF_4	F	97	96	80
6	[Rh(μ-Cl)(cod)]$_2$/(R)-Quinap	F	98	98	91.5
7	[Rh(cod)(R)-Quinap]BF_4	CF_3	77	95	38
8	[Rh(μ-Cl)(cod)]$_2$/(R)-Quinap	CF_3	72	90	66

[a] Standard conditions: substrate/borane = 1/1.1; cationic complex: 1 mol % [Rh(cod)(R)-Quinap]BF_4; neutral complex: 0.5 mol% [Rh(μ-Cl)(cod)]$_2$/ 2eq. (R)-Quinap. Solvent: THF. T: 25^{0}C. Time: 1h; [b] (R) Configuration determined by GC with chiral column FS-Cyclodex β-IP, 50m x 0.25mm.

The increase in asymmetric induction was highest in the hydroboration of the electron-poor vinylarene *p*-CF_3-styrene, where the enantioselectivity went from 38% with the cationic system to 66% with the neutral system. One example of improved enantioselectivity with neutral rhodium catalysts is also found in the related literature on the hydroboration of alkenylboronic esters, although the cationic rhodium catalyst provided better yields [37]. Nevertheless, no explanations were provided for these facts.

The neutralizing influence of chlorine as a coordinated counterion was confirmed in a new experiment in which different amounts of the salt $BnMe_3NCl$ were added to the catalytic system [Rh(cod)(R)-Quinap]BF_4, and the products of the hydroboration of styrene were distributed in a very similar way to when the neutral catalytic system was used, (Table 6, entries 1-3). An excess of chlorine does not even seem to be necessary. To obtain more information about the role of the halide in the asymmetric hydroboration reaction of vinylarenes, different additives containing the halide Cl^-, Br^-, I^- were introduced in the hydroboration of *p*-F-styrene, (Table 6, entries 4-6).

Table 6. Influence of the halide on asymmetric hydroboration/oxidation of vinylarenes with catecholborane, towards the (R)-sec-alcohol, catalysed by [Rh(cod)(R)-Quinap]BF_4.[a]



Entry	Additive	R	Yield (%)	Branched (%)	e.e [b] (%)
1	$BnMe_3NCl$ (0.012 mmol)	H	96	95	91
2	$BnMe_3NCl$ (0.03 mmol)	H	98	96	91.5
3	$BnMe_3NCl$ (0.05 mmol)	H	94	96	93
4	$BnMe_3NCl$ (0.03 mmol)	F	95	95	91.5
5	$PhMe_3NBr$ (0.03 mmol)	F	85	97.5	92
6	$PhMe_3NI$ (0.03 mmol)	F	95	95	91.5
7	$BnMe_3NCl$ (0.03 mmol)	CF_3	88	97	74
8	$BnMe_3NCl$ (0.03 mmol)	OMe	89.5	99	98

[a] Standard conditions: substrate/borane/Rh complex = 1/1.1/0.01. Solvent: THF. T: 25°C. Time: 1h; [b] (R) Configuration determined by GC with chiral column FS-Cyclodex β-IP, 50m x 0.25mm.

In the three cases, the increase in enantioselectivity was the same, despite the different electronic and steric factors of the halide. In terms of enantioselectivity,

the benefits of the chloride in the reaction media are very clear in the hydroboration of *p*-CF_3-styrene and *p*-MeO-styrene, (Table 6, entries 7 and 8). When the substrate was *p*-CF_3-styrene, the e.e value was 74%, which is only comparable with the asymmetric induction provided by the cationic rhodium complex modified with the closely heterotopic P,N ligand (S)-(+)-1-(2-di(2-furyl)phosphine-1-naphthyl)isoquinoline [9]. As far as the substrate *p*-MeO-styrene is concerned, its corresponding secondary alcohol was obtained with the highest enantiomeric excess reported so far in the literature, (e.e= 98%).

What is the role of the halide in the asymmetric induction of the hydroboration reaction of vinylarenes? This question leads to other questions about the nature and the structure of the neutral intermediate metal species involved in the catalytic cycle, and their influence on the catalytic activity. Despite the questions that remain unresolved for the hydroboration catalytic cycle, there is general agreement that the oxidative addition of the hydroborating reagent to the rhodium centre could be one of the first steps. The first B-H activation from neutral rhodium complexes was observed by Kono and Ito in 1975. They isolated the hydride-η^1-borylrhodium adduct **32**, [$Rh(PPh_3)_2HCl(Bcat)$], (Figure 14, where Bcat=catecholborane), from Wilkinson's catalyst, [23a].

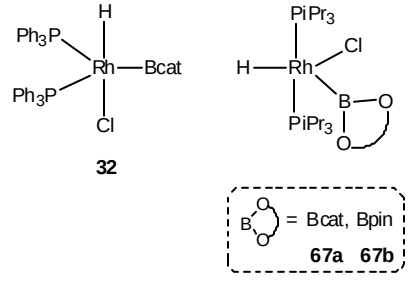


Figure 14

Recently, the relative location of the hydride and boryl in these neutral complexes was confirmed by the complete structural information provided by the analogue complexes [$Rh(P^iPr_3)_2HCl(Bcat)$] **67a** [23b] and [$Rh(P^iPr_3)_2HCl(Bpin)$] **67b**

[38] (Figure 14, where Bcat=catecholborane and Bpin=pinacolborane). However, to the best of our knowledge, the hydride-η^1-borylrhodium intermediates modified with chelating diphosphines have not been characterised and structurally determined. In this context and aimed to know the factors governing borane additions to Rh(I) centres, we studied the stoichiometric oxidative addition of catecholborane to the neutral catalytic system formed from $[Rh(\mu\text{-}Cl)(cod)]_2$ and 2eq. (L,L) (where (L,L)= Binap and Quinap). This study was conducted via multinuclear NMR techniques.

For the five coordinated, 16-electron hydride-η^1-borylrhodium complex formed, we can expect at least either a square-pyramid based (SP) or a trigonal bipyramid (TBP) geometry. However the resonances of the hydride ligand were shifted upfield and centred at δ = -15.82ppm as a double triplet, ($J_{H\text{-}Rh}$= 31.2Hz, $J_{H\text{-}P}$ = 16.2Hz), (Figure 15). This may indicate that the hydride position is cis to two equivalent phosphorous nuclei. The ^{31}P NMR agrees with the postulated equivalence of the phosphorous nuclei due to the unique doublet centered at 44.92ppm, ($J_{P\text{-}Rh}$= 197.8Hz), (Figure 15).

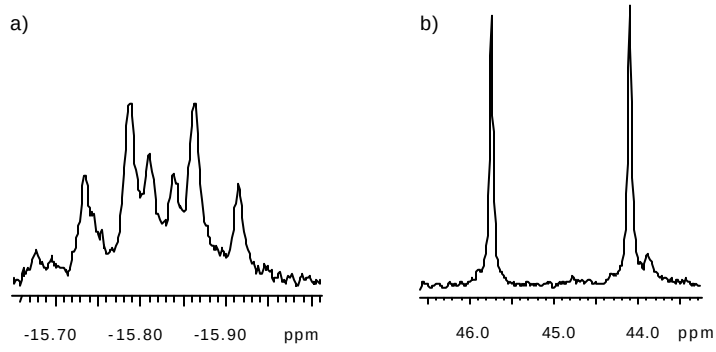


Figure 15.

(a) Hydride signal in the ^1H NMR of complex $[Rh(\mu\text{-}Cl)(cod)]_2$ after the addition of Binap and catecholborane; (b) ^{31}P NMR spectrum of the complex $[Rh(\mu\text{-}Cl)(cod)]_2$ after the addition of Binap and catecholborane.

This oxidative addition was confirmed by ^{11}B NMR, since the initial doublet due to the B bonded to H in free catecholborane (δ= 28.88ppm, $J_{B\text{-}H}$= 197.2Hz), was

shifted to a broad signal centred at δ= 23.20ppm. The equivalence of the phosphorous in the chelating diphosphine could be indicative of a TBP geometry where the bidentate ligand is located in the equatorial plane and the hydride ligand occupies the apical position. Since the hydride resonances are chemically shifted upfield and the oxidative addition of catecholborane is expected to be *cis*, we suggest a complete arrangement around the Rh(III) center, where the halide Cl^- is *trans* to the hydride and the boryl is in the equatorial plane, (Figure 16). Consistent spectroscopic values are also reported in a related study that describes the oxidative addition of catecholborane to [IrCl(CO)(L,L)] complexes, [27]. Taking into account that the following step in the catalytic cycle is the coordination of the alkene to the hydride-η^1-borylrhodium intermediate, we can envisage several different isomers with octahedral geometry. A systematic theoretical study, carried out by Bo and Daura, into the relative energies of these plausible isomers revealed that one of them could be the most stable.

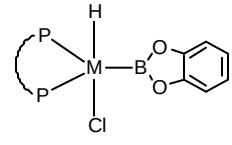


Figure 16

3. Conclusions

An NMR spectroscopic study of the stoichiometric addition of styrene and catecholborane addition to the catalyst precursor, $[Rh(cod)(L,L)]BF_4$ and $[Rh(cod)(\mu\text{-}Cl)]_2$/2eq (L,L), where (L,L)= (R)-Binap and (R)-Quinap, showed structural evidence for the intermediates that may be involved in the catalytic cycle.

A simple trend in the inductive electronic effect of the vinylarenes on the asymmetric induction is observed in the case the rhodium catalyst complex modified with (R)-Quinap and catecholborane or pinacolborane as a hydroborating reagent. The enantiomeric excess of the hydroborated/oxidised products increased as the electron withdrawing character of styrene substituents decreased: *p*-F-styrene < styrene < *p*-Me-styrene. However, this trend can not be extended to the rhodium complex modified with (R)-Binap.

Experimentally we found that the efficiency of the hydroborating reagent heavily depends on the steric factors of the catalytic systems. Thus, pinacolborane (stable and not sensitive to moisture) can be added to vinylarenes with selectivities similar to those of catecholborane, when the catalytic system is based on $[Rh(cod)(R)\text{-Quinap}]BF_4$. In contrast, a notable reversal of enantioselectivity can be achieved by using pinacolborane with $[Rh(cod)(R)\text{-Binap}]BF_4$.

The asymmetric hydroboration reaction catalysed by two transition metals (Rh and Ir), with the same *d* shell electronic configuration, shows considerable differences in both regio- and enantioselectivity. Cationic iridium complexes modified with (R)-Binap provide only 30% of the secondary alcohol with no enantiomeric excess. It would appear that, when the iridium complex is involved, significant steric influences come into play in the interaction between the metal complex, the substrate and the hydroborating reagent.

In addition to the efficiently catalysed hydroboration of vinylarenes by rhodium neutral systems, the enantioselectivity can be significantly enhanced. The beneficial neutralising effect of the coordinated chloride has been observed to come either from the catalyst precursor or from an additive such as R_3NCl. Similar benefits are observed when the nature of the halide is changed, from Cl^-, Br^-, to I^-. The increase in e.e values, which were as high as 98% for the hydroboration of *p*-MeO-styrene, were analysed in greater depth.

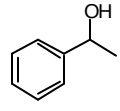
4. Experimental section

General comments. All reactions and handlings were carried out with standard vacuum line techniques under an atmosphere of dry nitrogen. All rhodium and iridium organometallic complexes were synthesised using standard Schlenk techniques. All organic solvents were distilled, stored over molecular sieve (0.4 nm Aldrich), and degassed with a nitrogen flow prior to use. The complexes $[M(\mu\text{-Cl})(cod)]_2$ [39], $[M(cod)_2]BF_4$ [40-41], $[M(cod)(R)\text{-Binap}]BF_4$ [42], (where M=Rh, Ir) and $[Rh(cod)(R)\text{-Quinap}]BF_4$ [9], were prepared as previously reported. They were characterized by elemental analysis, ^1H and ^{31}P NMR, and FTIR. NMR spectra were recorded on a Varian Gemini 300 and Mercury 400 spectrometer. Chemical shifts were reported relative to tetramethylsilane for ^1H as internal reference, 85% H_3PO_4 for ^{31}P and BF_3OEt_2 for ^{11}B as the external reference. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 II with a flame ionisation detector equipped with a chiral column FSCyclodex β-IP, 50m x 0.25mm. Elemental analysis of organometallic complexes was carried out on a Carlo-Erba Microanalyzer EA 1108. IR spectra (range 4000-400cm^{-1}) were recorded on a FTIR MIDAC PROSPECT-IR spectrometer with KBr pellets.

Experimental NMR studies. The stoichiometric addition of styrene and catecholborane to the precursor of catalyst $[Rh(cod)(L,L)]BF_4$ and $[Rh(\mu\text{-Cl})(cod)]$/ 2eq. (L,L), where (L,L) = (R)-Binap and (R)-Quinap, was carried out in CD_3CN solvent and monitored by ^1H, ^{31}P and ^{11}B NMR. An orange solution of the catalyst precursor $[Rh(cod)(L,L)]BF_4$ (0.016 mmol) and $[Rh(\mu\text{-Cl})(cod)]$/2eq. (L,L) (0.08 mmol) in CD_3CN (0.7mL) was prepared under nitrogen in a NMR tube. It was monitored by ^1H and ^{31}P NMR. The styrene (0.016mmol, 1.8μL) was added to the solution of the catalyst precursor under nitrogen. ^1H, ^{31}P NMR spectra were observed. Freshly distilled catecholborane (0.016mmol) was added under nitrogen and then the solution changed colour from yelow to brown. The mixture was monitored by ^1H, ^{31}P and ^{11}B NMR. Previously, ^1H NMR spectrum of styrene and ^{11}B NMR spectrum of freshly distilled catecholborene were carried out in CD_3CN solvent.

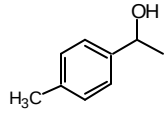
Homogeneous catalytic hydroboration/oxidation of vinylarenes with catecholborane. Vinylarene (2 mmol) was added to a solution of catalyst (1 mol%) inTHF (2 mL) under nitrogen. The solution was stirred for 5 min and freshly distilled catecholborane (2 mmol) was then added. The mixture was stirred at ambient temperature for 1h and then quenched with EtOH (2 mL). Work up was carried out carefully because of the risk of explosion by using peroxides with ether and THF. Afterwards, NaOH (2M, 2mL) and H_2O_2 (2 mL) were added and the mixture was stirred for several hours. The reaction mixture was extracted with Et_2O (3x20) and washed (NaOH 2M, H_2O, saturated brine). The organic extracts were dried over $MgSO_4$, and evaporated under reduced pressure. The products were characterised by NMR, and quantification was carried out by gas chromatography.

Phenylethanol [8a]



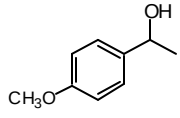
^{1}H RMN δ(ppm)= 7.50-7.20 (m ,5H), 4.55 (q ,$^3J_{H-H}$=6.7Hz, 1H), 1.80(br s, 1H), 1.50 (d ,$^3J_{H-H}$=6.6Hz, 3H).

1-(4-Methylphenyl)ethanol [9]



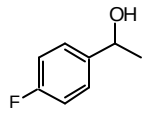
^{1}H RMN δ(ppm)= 7.29 (d ,$^3J_{H-H}$=8.2Hz, 2H), 7.19 (d, $^3J_{H-H}$= =8.2Hz, 2H), 4.86 (q ,$^3J_{H-H}$=6.6Hz, 1H), 2.36 (s, 3H), 1.80(br s, 1H), 1.48 (d ,$^3J_{H-H}$=6.6Hz, 3H).

1-(4-Methoxyphenyl)ethanol [9]



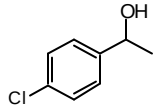
^{1}H RMN δ(ppm)= 7.31 (d ,$^3J_{H-H}$=8.2Hz, 2H), 6.9 (d ,$^3J_{H-H}$= =8.2Hz, 2H), 4.87 (q ,$^3J_{H-H}$=6.5Hz, 1H), 3.82 (s, 3H), 1.74(br s, 1H), 1.48 (d, $^3J_{H-H}$=6.5Hz,3H).

1-(4-Fluorophenyl)ethanol [9]



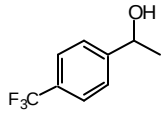
^{1}H RMN δ(ppm)= 7.40-7.10 (m, 4H), 4.86 (q ,$^{3}J_{H-H}$=6.4Hz, 1H), 1.90(br s, 1H), 1.48 (d , $^{3}J_{H-H}$=6.4Hz, 3H).

1-(4-Chlorophenyl)ethanol [9]



^{1}H RMN δ(ppm)= 7.40-7.10 (m, 4H), 4.85 (q ,$^{3}J_{H-H}$=6.6Hz, 1H), 1.70(br s, 1H), 1.47 (d , $^{3}J_{H-H}$=6.6Hz, 3H).

1-(4-Trifluoromethylphenyl)ethanol [9]



^{1}H RMN δ(ppm)= 7.7-7.4 (m, 4H), 4.97 (q ,$^{3}J_{H-H}$=6.6Hz, 1H), 1.80 (br s, 1H), 1.51 (d , $^{3}J_{H-H}$=6.5Hz, 3H).

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