

Chapter 3

Recovery of the catalyst

Recently there has been considerable interest in the heterogenisation of chiral homogeneous catalytic systems. Many reports have shown that it is possible to design and produce new chiral catalytic system that has obvious advantages over their soluble counterparts: they can induce asymmetry, they can be removed from the reaction mixture by simple filtration and, in many cases, they can be recycled and used again.

This chapter describes, for the first time, the rhodium and iridium chiral complexes immobilised on either natural or synthetic solid supports, to be applied in the catalytic asymmetric hydroboration reaction of vinylarenes.

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1. Introduction

The catalytic asymmetric hydroboration reaction provides a way of transforming alkenes into optically enriched organoboron adducts, C*-B. The oxidation of the chiral organoboron, (via $\text{H}_2\text{O}_2/\text{OH}^-$), achieves the respective alcohol C*-OH with complete retention of the configuration.

When turnover is complete in the catalytic hydroboration of vinylarenes, with most rhodium complexes modified with bidentate chiral ligands, the resting state of the catalyst decomposes as a result of its instability. In recent times, in an attempt to be able to reuse the catalytic system several times, Grützmacher and coworkers have synthesised an air-stable polycyclic phosphirane ligand called BABAR-Phos which after modifying a cationic rhodium complex **68**, (Figure 1), provides a more stable resting state which continues hydroborating after the re-addition of alkenes [1]. There was no decrease in catalytic activity even after five catalytic cycles. However, the BABAR-Phos rhodium complex **68** has the drawback that the catalyst is destroyed during the workup that provides the corresponding alcohols, because this is done in a $\text{H}_2\text{O}_2/\text{OH}^-$ medium.

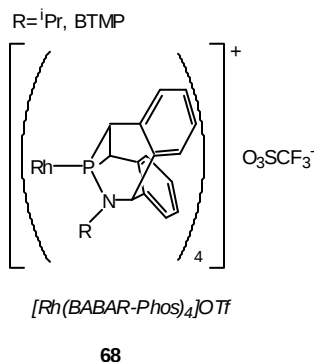


Figure 1

Therefore, the destruction of the catalyst during the workup should be prevented by separation before the oxidation. This would guarantee the stability of the catalytic system and make it possible for it to be reused in new consecutive hydroboration reactions.

It has been mentioned above that the catalytic system Rh(I) modified with phosphinamine Quinap provides high regio- and enantioselectivity towards the hydroboration/oxidation of vinylarenes and β -substituted vinylarenes working at room temperature [2]. The catalytic systems based on Rh(I) with the analogous diphosphine ligand Binap gave high regioselectivity but only moderate enantioselectivity under the same reaction conditions for the catalytic hydroboration reaction [3]. However, the instability of the resting state of both homogeneous catalyst and the difficulty of separating and recycling the expensive chiral rhodium complexes are still serious disadvantages. A recent report has described that an atropoisomeric P,N ligand which is configurationally stable in an acidic medium, Pyphos (**31**), can be recovered from the solution through the acid/aqueous extraction of the pyridine moiety of the P,N ligand [4]. This meant that the recovery of the expensive chiral ligand was also a possibility. However it should be pointed out that the totality of the P,N ligand cannot be recovered and that the transition metal complex cannot be recovered at all. In view of these limitations, the problem of developing a method for separating, recovering and reusing metal complexes modified with chiral ligands from a catalytic process remains unresolved.

The advantages of immobilising the homogeneous catalyst on a heterogeneous support are that separation is straightforward and the catalyst can be reused. The activities and selectivities are similar to those of homogeneous systems. Indeed, all these properties are particularly significant for the economic viability of the process, especially when sophisticated chiral ligands are involved, [5, 6]. Of the different immobilisation procedures, the non-covalent grafting of homogeneous chiral cationic catalysts on solid supports could be an interesting alternative, because it is efficient and easy to prepare.

From our experience [7], we became interested in immobilising catalytic systems in clay structures through absorption or cationic exchange, which is an easy and clean alternative to heterogenisation. We attempted to immobilise optically pure

rhodium (I) complexes, $[M(\text{cod})(L,L)]X$ where $(L,L) = (R)\text{-Binap}, (S)\text{-Quinap}, (S,S)\text{-bdpp}$; $M = \text{Ir}$ or Rh ; $X = \text{BF}_4, \text{PF}_6, \text{BPh}_4, \text{OTf}$, (Figure 2), through adsorptive forces onto natural clay structures (montmorillonite K-10) and through electrostatic forces into natural smectites (bentonites) [8,9] or on synthetic organo(bis-silantriolates) [10].

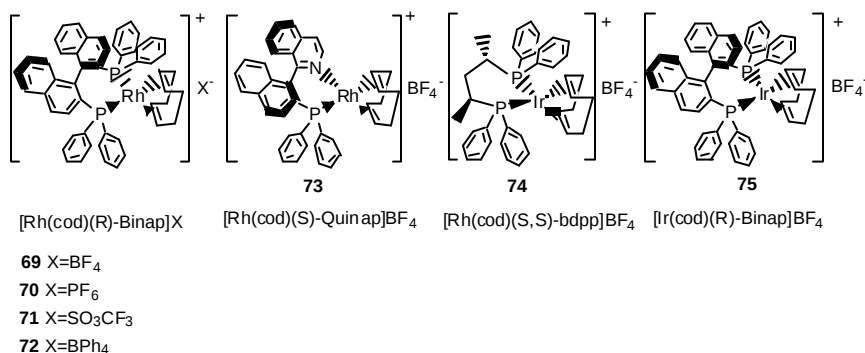


Figure 2

2. Results and discussion

2.1. Heterogenised catalytic hydroboration using natural supports

2.1.a. Study of the immobilisation process

We immobilised the organometallic complexes $[M(\text{cod})(L,L)]X$ ($M = \text{Rh}$ and Ir ; $(L,L) = (R)\text{-Binap}, (S,S)\text{-bdpp}, (S)\text{-Quinap}$; $X = \text{BF}_4, \text{PF}_6, \text{SO}_3\text{CF}_3, \text{BPh}_4$), (Figure 2), onto the clays montmorillonite K-10 (MK-10) and bentonite (BDH), by the previously described solvent-impregnation method [11]. Coloured solutions of the ionic complexes in anhydrous dichloromethane were stirred with the solid support for 24 h under nitrogen. The amount of metal complex $[\text{Rh}(\text{cod})(\text{R})\text{-Binap}]\text{BF}_4$ (**69**) adsorbed by the clay was determined by gravimetric analysis in which the difference between the weights of the complex before and after the immobilisation was measured, (Table 1). These data suggest that when the montmorillonite K-10 was predried for 24 h at 100°C

(MK-10_T), the amount of rhodium complex **69** adsorbed onto the clay was higher because any adsorbed water could be eliminated. However, when the montmorillonite K-10 was calcined to 400⁰C, the resulting calcined solid (MK-10₄₀₀) did not adsorb more rhodium complex than MK-10_T, probably because of the loss of interlamellar water which resulted in layer collapse. The dehydroxylation process during the calcinations modifies the residual microporosity and the values of the BET surface area from 221 m²g⁻¹ for MK-10_T to 211 m²g⁻¹ for MK-10₄₀₀. Similar behaviour was observed in the immobilisation process of [M(cod)(PPh₃)₂]BF₄ (M= Ir and Rh) onto clays in previous study [7b].

The percentages of rhodium complexes with other counterions (X=PF₆, SO₃CF₃, BPh₄) adsorbed onto MK-10_T were very similar (Table 1). Conductimetric and ¹⁹F and ¹¹B NMR analyses of the liquid filtrate after the impregnation process indicated that the counterions (BF₄, PF₆, SO₃CF₃, BPh₄) were not present in the filtrates, presumably because they were adsorbed on the support.

Table 1. Amounts of immobilised metal complexes [M(cod)(L,L)]X on the clays.

Solid ^[a]	Heterogenised catalytic system	mmol complex per g solid ^[b]
MK-10	69 -MK-10	0.055
MK-10 _T	69 -MK-10 _T	0.084
MK-10 ₄₀₀	69 -MK-10 ₄₀₀	0.058
BDH _T	69 -BDH _T	0.046
MK-10 _T	70 -MK-10 _T	0.074
MK-10 _T	71 -MK-10 _T	0.085
MK-10 _T	72 -MK-10 _T	0.062
MK-10 _T	73 -MK-10 _T	0.092
MK-10 _T	74 -MK-10 _T	0.093

[a] MK-10: commercial montmorillonite K-10; MK-10_T: preheated at 100⁰C for 24 h; MK-10₄₀₀: previously calcined at 400⁰C for 3 h; BDH_T: commercial bentonite preheated at 100⁰C for 24 h; [b] Calculated from the equation [(mg initial complex-mg final complex)/molecular weight complex]/(g solid + g adsorbed complex).

Powder X-ray diffraction (XRD) is very useful technique for characterising of heterogenised organometallic systems [7c], [12-13]. This method shows how the basal distance between the layers varies in relation to the position of the (001) reflection peak.

It is known that although both montmorillonite K-10 (MK-10) and bentonite (BDH) are the same montmorillonite clay material, their crystallinity is significantly different [9]. The powder X-ray diffractograms of BDH and MK-10 do not show significant differences in the characteristics peaks associated with the (001) reflection, although the peaks are better defined when BDH is the support. This suggests that the bentonite has a major laminar ordination, or crystallinity, (Figure 3). In fact MK-10 is prepared from BDH by acid treatment, which partially destroys the bentonite layer structure. This disorders the BET surface area and increases it from $53 \text{ m}^2\text{g}^{-1}$ to $221 \text{ m}^2\text{g}^{-1}$, favouring the adsorption properties in MK-10 in contrast to cation exchange in BDH.

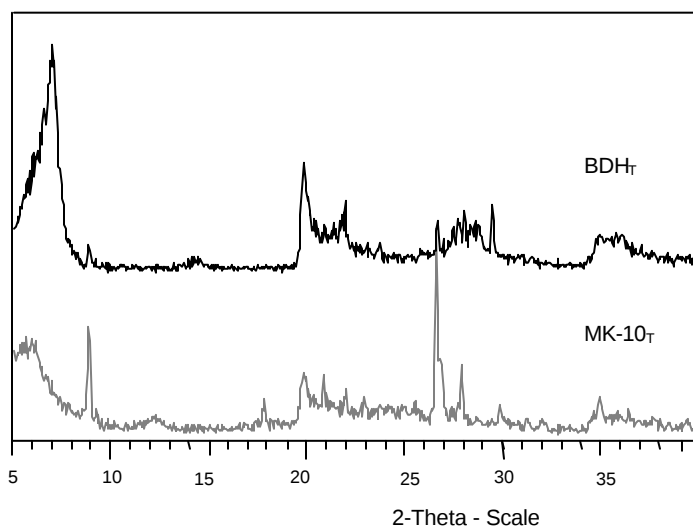


Figure 3

The powder-X-ray diffractogram of BDH_T , MK-10_T Fluka; montmorillonite (n° 15-0135 in JCPDS-ICDD), flogopite (n° 16-0344 in JCPDS-ICDD), quartz (n° 33-1161 in JCPDS-ICDD).

In fact, there was a noticeable difference when preheated bentonite (BDH_T) was used as support. Following the same impregnation procedure, the amount of metal complex **69** adsorbed was only 0.046mmol per gram of clay, (Table 1). This data is in agreement with the fact that the surface area of BDH (53 m²g⁻¹) is smaller than that of MK-10. Also, conductimetric analyses made after washing the immobilised catalytic system in bentonite revealed the presence of ionic species, which indicate that immobilisation took place mainly through a cation exchange process rather than adsorption. The powder X-ray diffraction data showed an insignificant shift in the (001) diffraction line on the diffractogram between MK-10_T and **69**-MK-10_T, but a basal distance that increased from 12.3 Å in BDH_T to 16 Å in **69**-BDH_T, (Figure 4).

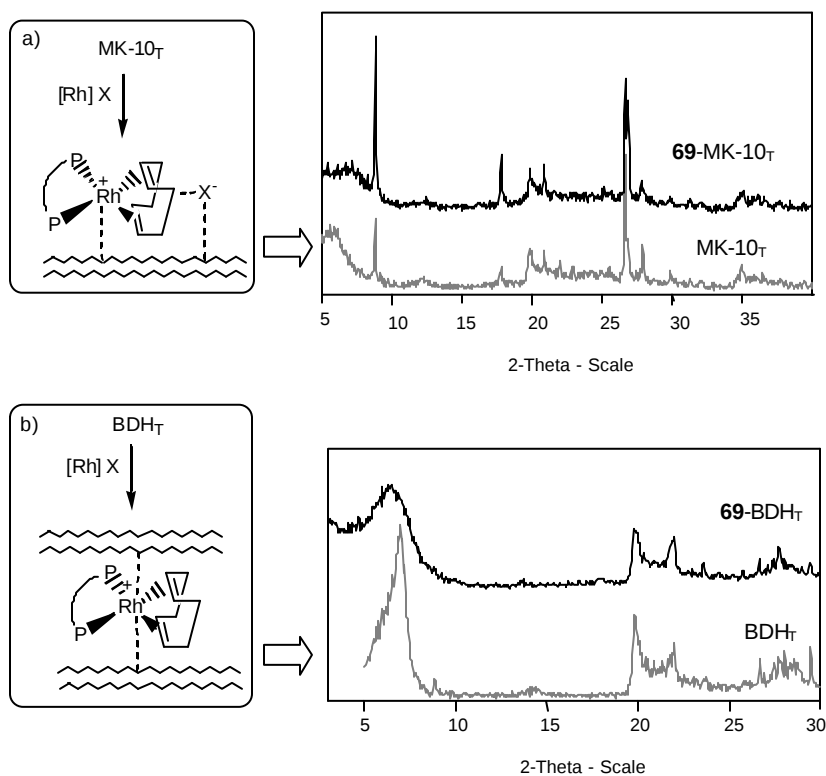


Figure 4

We recorded ^{19}F , ^{31}P and ^{11}B NMR spectra in CDCl_3 during the impregnation process. These experiments provided evidence that MK-10 $_{\text{T}}$ could adsorb ionic metal complexes through the cationic and anionic counterparts. In contrast, the immobilisation of the same complexes into bentonite occurred through only the cation counterpart by ionic exchange.

The ^{19}F NMR spectrum of **69** had two singlets at $\delta = -154.20$ and -154.30 ppm with an intensity ratio of 1:4, which is consistent with the isotopic distribution between ^{19}F and ^{10}B and ^{11}B , respectively (Figure 5b), while the ^{31}P spectrum has a doublet at $\delta = 26.21$ ppm ($J_{\text{P-Rh}} = 145.4$ Hz) (Figure 5a). The intensity of these signals decreases significantly in the ^{31}P and ^{19}F NMR locked spectra of a slurry in CDCl_3 when MK-10 $_{\text{T}}$ is added little by little to complex **69** (Figure 6). This is because the concentration of **69** decreases in solution during the immobilisation process. To ensure that the disappearance of the signals was not caused by a shimming problem in the presence of the solid, we carried out the above experiments with the addition of an inert reactant, such as the free ligand Binap (10 mg). Figure 5a and Figure 6a show that after the consecutive addition of MK-10 $_{\text{T}}$, the intensity of the doublet ($\delta(^{31}\text{P}) = 26.40$ ppm) due to P nuclei from the coordinated Binap ligand decreases significantly in comparison with that of the singlet due to the free Binap ligand ($\delta(^{31}\text{P}) = -14.60$ ppm). This is in agreement with the fact that complex **69** is being immobilised onto MK-10 $_{\text{T}}$.

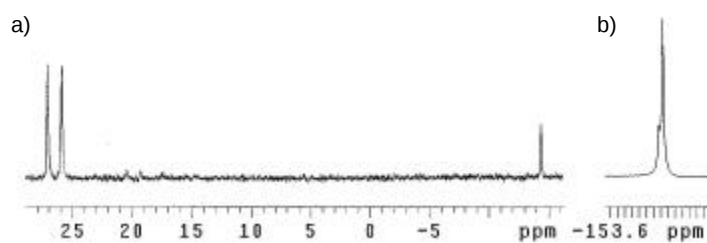


Figure 5

a) ^{31}P NMR spectra of 20 mg of **69** in CDCl_3 + 10 mg of free Binap; b) ^{19}F NMR spectra of 20 mg of **69** in CDCl_3 .

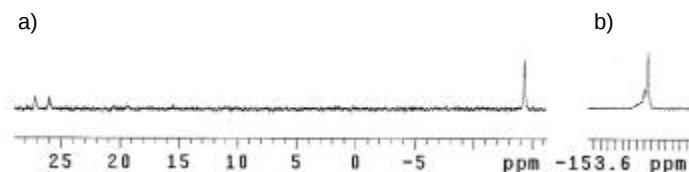
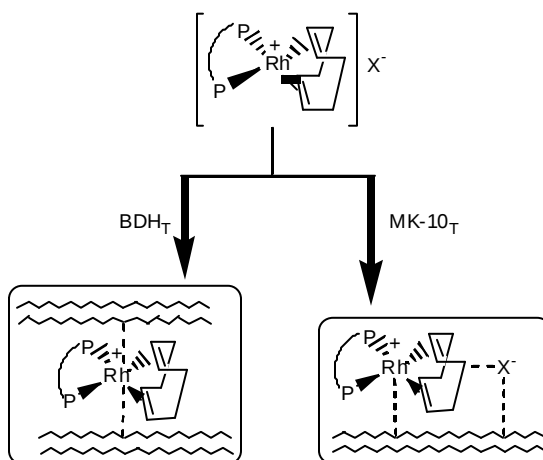


Figure 6

a) ^{31}P NMR spectra of 20 mg of **69** in CDCl_3 + 10 mg of free Binap + 100 mg of MK-10 $_{\text{T}}$; b) ^{19}F NMR spectra of 20 mg of **69** in CDCl_3 + 100 mg of MK-10 $_{\text{T}}$.

Because both nuclei (F and P) were affected in the immobilisation process, we suggest that the two ionic parts of the metal complex may interact with MK-10 $_{\text{T}}$ through weak forces such as electrostatic and/or hydrogen bonding interactions (Scheme 1). The fact that both, the cation and anion counterparts, from the complex seem to be adsorbed onto the solid implies a new concept which differs from the other supported hydrogen-bonded catalysts previously reported in the literature in which immobilisation mainly takes place in a monodentate way between the terminal silanols



Scheme 1

of different types of silica and the oxygen atom of sulfonate groups from phosphine ligands contained in the zwitterionic rhodium(I) complexes [14] and [15] or from triflate

counteranions of cationic ruthenium(II) [16] and rhodium(I) [12], [15] complexes. Unfortunately, as the loading level of the immobilised complexes was low, we could not confirm the presence of hydrogen bonding by IR spectroscopy.

Therefore, taking into account the lack of supporting experimental data, we can only suggest that the nature of the interactions between the solid and complex **69** could be due to weak forces such as electrostatic and/or hydrogen bonding.

The MAS ^{31}P NMR spectrum of the grafted complex **69**-MK-10 τ is shown in Figure 7.b. It consists of a broad signal centred at $\delta = 30.00\text{ppm}$. The CP MAS ^{31}P NMR spectrum of the unsupported complex **69** has a double doublet centred at $\delta = 28.00\text{ppm}$ (Figure 7.a). Comparison of the two solid-state NMR spectra suggests that they are highly similar and thus consistent with the immobilisation of the complex onto montmorillonite K-10.

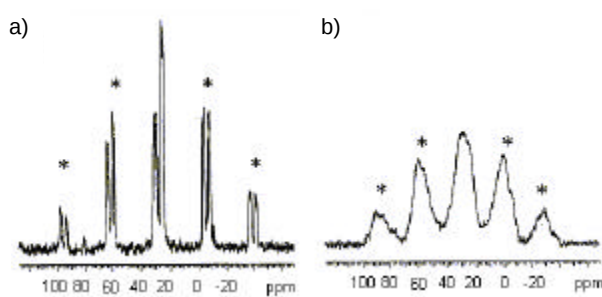


Figure 7

a) CP MAS ^{31}P NMR spectrum of $[\text{Rh}(\text{cod})(\text{R})\text{-Binap}]\text{BF}_4$ (**69**); b) MAS ^{31}P NMR spectrum of $[\text{Rh}(\text{cod})(\text{R})\text{-Binap}]\text{BF}_4/\text{MK-10}\tau$. Spinning side bands are denoted by asterisks.

Similar spectroscopic features have been observed during the immobilisation of $[\text{Rh}(\text{cod})(\text{R})\text{-Binap}]\text{PF}_6$ **70**, $[\text{Rh}(\text{cod})(\text{R})\text{-Binap}]\text{SO}_3\text{CF}_3$ **71**, and $[\text{Rh}(\text{cod})(\text{R})\text{-Binap}]\text{BPh}_4$ **72** onto MK-10 τ . With **70-72**, the intensity of the signals decreased significantly on the ^{19}F , ^{31}P , ^{11}B NMR locked spectra of the slurry obtained by consecutively addition of MK-10 τ to a CDCl_3 solution of the complexes. It is noteworthy that the counteranion BPh_4 is also adsorbed onto MK-10 τ according to the

disappearance of the singlet attributed to B nuclei in the ^{11}B NMR locked spectra of the slurry obtained by the consecutive addition of MK-10 $_{\text{T}}$ to a solution of complex **72** (Figure 8.b and d). The adsorption of lipophilic counteranions has not been previously observed in analogue immobilisation processes onto MCM-41 of ionic rhodium complexes containing BAr_F as counteranion [12].

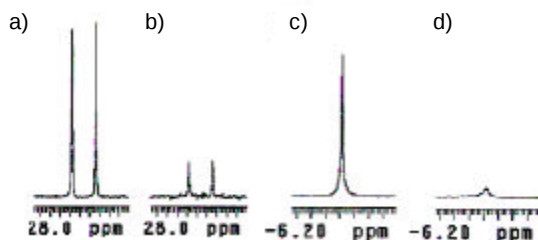


Figure 8

^{31}P NMR spectrum of a) 20 mg of $[\text{Rh}(\text{cod})(\text{R})\text{-Binap}]\text{BPh}_4$ (**72**) in CDCl_3 ; b) slurry of a) + 125 mg of MK-10 $_{\text{T}}$. ^{11}B NMR spectrum of c) 20 mg of **72** in CDCl_3 ; d) slurry of c) + 125 mg of MK-10 $_{\text{T}}$.

A significant difference was observed between the ^{19}F and ^{31}P NMR experiments carried out during the immobilisation process of **69** into BDH $_{\text{T}}$. While the intensities of the signals of ^{31}P NMR spectra decrease significantly when BDH is added, (Figure 9.a and b), the intensities of the signals in the ^{19}F NMR spectra did not change throughout the addition (Figure 9.c and d). The reduction of the signals in the ^{31}P spectra during the impregnation process suggests that the cationic counterpart of complex **69** is no longer in solution. Therefore, the counteranion could be immobilised into the solid through cation exchange. This agrees with the ^{19}F NMR spectra, in which the intensity of the signals for F nuclei from BF_4^- did not decrease during the impregnation process. This shows that it might remain mainly in the solution, probably as MBF_4 (where M is the interlamellar metal cation from BDH $_{\text{T}}$), after the cation exchange with $[\text{Rh}(\text{cod})(\text{R})\text{-Binap}]^+$ (Scheme 1).

In summary, the mechanism for grafting the ionic complexes to MK-10 τ and BDH τ seems to be different. In the first case, we suggest that the kind of interaction between the counteranion and counteranion to MK-10 τ could be due to weak forces,

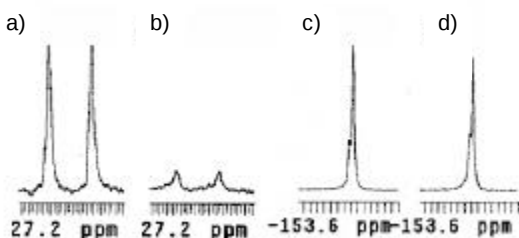


Figure 9

^{31}P NMR spectrum of: a) 20 mg of **69** in CDCl_3 ; b) slurry of a) + 125 mg of BDH τ . ^{19}F NMR spectrum of: c) 20 mg of **69** in CDCl_3 ; d) slurry of c) + 125 mg of BDH τ .

such as electrostatic and/or hydrogen bonding, but in the second case the electrostatic attraction between the counteranion and the bentonite layers could be the significant feature of this immobilisation. The different ways in which these catalysts are grafted on the clays could also lead to further differences in the activities and selectivities when they are used as catalytic systems in the asymmetric hydroboration of vinylarenes.

2.1.b. Study of the heterogenised catalytic hydroboration

At this point we focused on the potential catalytic activity of the immobilised system towards the asymmetric hydroboration of vinylarenes. We first concentrated our efforts on a model reaction with styrene as substrate. In order to consider the most important parameters that affect this asymmetric transformation, (Chapter 2), we also studied the influence of the counteranion, the chiral ligand, the metal and the support. Once the heterogenised process had been optimised, we extended the study to other substrates with significant electron differences.

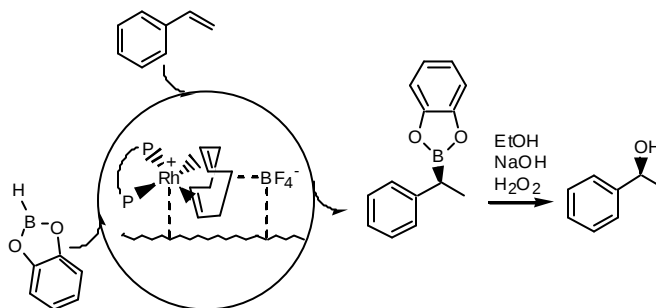
We started by examining the catalytic properties of the model rhodium complex $[\text{Rh}(\text{cod})(\text{R})\text{-Binap}]\text{BF}_4$, (**69**), adsorbed on commercial montmorillonite MK-10. In the homogeneous hydroboration/oxidation of styrene, the catalyst precursor **69** provides high yields and regioselectivities for 1-phenylethanol, but only moderate enantiomeric excesses [3], (Table 2, entry 1). This behaviour justifies our choice of this catalytic system, since it can reveal any increase [7b], [17] or decrease in the stereoselectivity induced by the supported catalyst.

Table 2. Asymmetric hydroboration/oxidation of styrene towards (R)-(+)-1-phenylethanol catalysed by the immobilised $[\text{Rh}(\text{cod})(\text{R})\text{-Binap}]\text{BF}_4$, (**69**).^[a]

Entry	Heterogenised catalytic system	Run (%)	Yield (%)	Branched (%)	e.e. ^[b] (%)
1	69	1	92	99	57
2	69 -MK-10	1	41	92	47
3	69 -MK-10 _T	1	96	97	55
		2	99	97	60
4	69 -BDH _T	1	26	35	5
		2	94	63	35

[a] Standard conditions: styrene/catecholborane/Rh complex=1:1.1:0.02. Solvent: THF. T: 25°C. Time: 2 h; [b] *R* configuration determined by GC with chiral column FS-Cyclodex β -IP, 50 m x 0.25 mm.

Once the solid-supported catalyst had been prepared, it was tested for activity, regioselectivity, enantioselectivity, resistance to degradation and reusability in the hydroboration/oxidation of the model substrate styrene (Scheme 2). To compare the



Scheme 2

activity and stability of the supported catalyst with its homogeneous counterpart, we performed the hydroboration of styrene under standard conditions: styrene/catecholborane/Rh=1:1.1:0.02, THF as solvent, 25°C, 2 h. As can be seen in Table 2, the activity and selectivity of catalyst **69**-MK-10 was lower than those of the homogeneous catalytic system under the same reaction conditions (Table 2, entries 1 and 2). The significant amount of interlamellar water in montmorillonite could have favoured the degradation of catecholborane and/or the transition metal complex. ^{11}B NMR experiments carried out on MK-10 and catecholborane over the time scale of the catalytic experiment showed that the doublet at $\delta(^{11}\text{B}) = 26.50\text{ppm}$ from catecholborane decreases in intensity as a new broad signal emerges at $\delta(^{11}\text{B}) = 20.00\text{ppm}$, which can be attributed to the catecholboronate acid formed. However, when the montmorillonite was heated to at least 100°C before the immobilisation of **69**, the activity and selectivity of the resulting supported catalytic system **69**-MK-10 $_{\text{T}}$ were similar to those of the homogeneous system. The supported catalyst was removed by filtration under inert atmosphere and repeated catalytic hydroborations were carried out without loss of activity or selectivity (Table 2, entry 3). Leaching of the rhodium complex was not considered because no product was formed when styrene and catecholborane were added to the filtrate of the first run. We found significant differences in the hydroboration/oxidation of styrene when we prepared the supported catalytic system from the preheated clay bentonite BDH $_{\text{T}}$ and complex **69**, (Table 2, entry 4). The closed environment of complex **69** immobilised mainly in the internal surface of the bentonite may be different to that of complex **69** grafted onto the external surface of

montmorillonite K-10. The low conversion and selectivity of the branched product may be related to the restricted diffusion of the substrate, reactant and product, although the activity improves slightly in the second consecutive run.

The MAS ^{31}P NMR spectrum of the solid **69**-MK-10 $_{\text{T}}$ that was recovered after two consecutive runs had a broad signal centred at 30.00ppm (Figure 10). If compared with Figure 7.a and b, this is consistent with the permanence of complex **69** or a closed Rh-Binap complex involved in the reaction, which is immobilised onto the MK-10 $_{\text{T}}$.

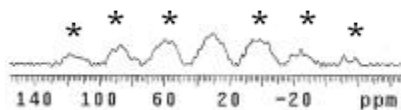


Figure 10

MAS ^{31}P NMR spectrum of **69**-MK-10 $_{\text{T}}$ after two consecutive runs. Spinning side bands are denoted by asterisks.

Influence of the counteranion. In an attempt to rationalise the catalytic activity exhibited by the supported rhodium complex **69**-MK-10 $_{\text{T}}$, (Figure 11), we decided to extend our

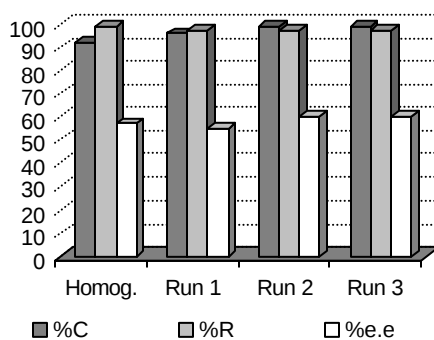


Figure 11

Catalytic activity provided by
[Rh(cod)(R)-Binap]BF $_4$ (**69**) in the

homogeneous and heterogenised
hydroboration of styrene.

study to a wider variety of cationic rhodium complexes with different counteranions, such as $[\text{Rh}(\text{cod})(\text{R})\text{-Binap}]\text{X}$ ($\text{X} = \text{PF}_6$, SO_3CF_3 , and BPh_4). We therefore immobilised complexes **70-72** onto MK-10 τ following the same impregnation procedure described above. The immobilised complex **71** was found to provide the same activity and selectivity as the unsupported complex **71**. It also provided recoverability of at least three consecutive runs in the hydroboration/oxidation of styrene, which was used as the test substrate (Figure 12). Additional insight into a slight enhancement of the enantioselectivity by using the triflate anion is also noteworthy. It has already been reported in the literature that the presence of anions such as sulfonate enhances asymmetric catalysis [13].

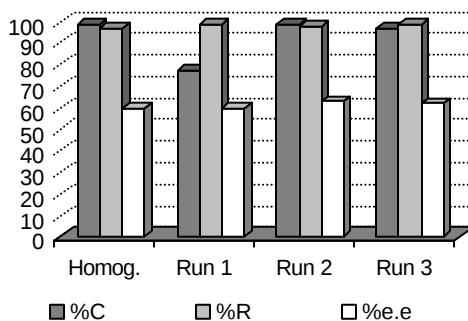


Figure 12

Catalytic activity provided by $[\text{Rh}(\text{cod})(\text{R})\text{-Binap}]\text{SO}_3\text{CF}_3$ (**71**) in the homogeneous and heterogenised hydroboration of styrene.

The recyclability of the immobilised catalytic system **70**-MK-10 τ is also demonstrated (Figure 13), although the selectivity decreased slightly after the third

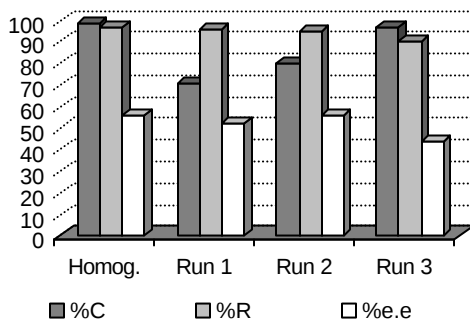


Figure 13

Catalytic activity provided by $[\text{Rh}(\text{cod})(\text{R})\text{-Binap}]\text{PF}_6$ (**70**) in the homogeneous and heterogenised hydroboration of styrene.

consecutive run. The reduction of the regio- and enantioselectivities with this system may be because the immobilised catalytic system is less stable when the counteranion PF_6 is involved.

We observed similar features when the ionic iridium catalytic system $[\text{Ir}(\text{cod})(\text{PPh}_3)_2]\text{X}$ ($\text{X} = \text{PF}_6$ or BF_4) was tested in the hydrogenation of imines **[7a]**. Even more striking was that the regio- and enantioselectivities provided by the immobilised catalytic system **72-MK-10_T** were greater than those of its homogeneous counterpart (Figure 14). The proven tendency of BPh_4 to form π -complexes and tight ion pairs [18]

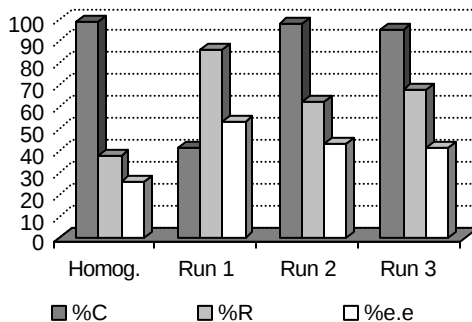


Figure 14

Catalytic activity provided by [Rh(cod)(R)-Binap]BPh₄ (**72**) in the homogeneous and heterogenised hydroboration of styrene.

might be the cause of the low regio- and enantioselectivities provided by the homogeneous catalytic system **72**. Immobilisation of both the cationic and anionic counterparts of **72** onto montmorillonite K-10 seems to be beneficial for the hydroboration reactions, probably because the counteranion is prevented from coordinating to the metal [18g]. However, although the regio- and enantioselectivities are higher than with the homogeneous version, they do not reach the selectivity of the supported catalytic systems where X= PF₆, SO₃CF₃ and BF₄.

Influence of the ligand. We made a comprehensive study of several ligands including (S,S)-bdpp and (S)-Quinap, to determine how they affect the hydroboration/oxidation of styrene. The use of (S,S)-bdpp as chiral ligand can provide four possible conformers of a six-membered chelate ring when it is coordinated to a metal [19]. Two of these conformers are achiral chair conformations with the phenyl rings in an achiral array, and the other two conformers are chiral δ -skew conformations. We wondered whether immobilising a rhodium complex modified with (S,S)-bdpp would favour the formation of any one of these conformers and modify the low asymmetric induction provided by the homogeneous catalytic system. Thus, we carried out the hydroboration/oxidation of styrene with [Rh(cod)(S,S)-bdpp]BF₄, (**74**), and the grafted complex **74**-MK-10_T. There was no significant difference between the catalytic behaviour of the homogeneous version and that of the heterogenised version. The activity and regioselectivity of 1-phenylethanol from complex **74** were high, but the enantioselectivity was low and was reproduced with **74**-MK-10_T after the second consecutive run (Table 3, entries 1 and 2).

Table 3. Asymmetric hydroboration/oxidation of styrene towards (S)-(-)-1-phenylethanol catalysed by the immobilised [Rh(cod)(L,L)]BF₄.^[a]

Entry	Heterogenised catalytic system	Run (%)	Yield (%)	Branched (%)	e.e. ^[b] (%)
-------	--------------------------------	---------	-----------	--------------	-------------------------

1	74	1	98	98	20
2	74 -MK-10 _T	1	82	87	14
		2	97	94	19
3	73	1	99	95	88
4	73 -MK-10 _T	1	51	68	50
		2	98	97	89
		3	92	97	86
		4	98	98	88

[a] Standard conditions: styrene/catecholborane/Rh complex=1:1.1:0.02. Solvent: THF. T: 25°C. Time: 2 h; [b] S configuration determined by GC with chiral column FS-Cyclodex β -IP, 50 m x 0.25 mm.

The other interesting ligand which chelates with the metal to form a six-membered ring is Quinap. This P,N ligand is less bulky than its parent ligand Binap in the region of the isoquinoline because one of the diphenylphosphinonaphthalene moieties has been replaced. This structural difference, in addition to the electronic features of the P,N ligand, explains why the asymmetric induction is higher with chiral Quinap than with Binap [2]. Other axially chiral P-N ligands, such as Phenap (**29**) [20], 2-Ph-quinazolinap (**30**) [21] and Pyphos (**31**) [4], have been developed over the last few years for use in the hydroboration of vinylarenes. However, optimised values for the regioselectivities of the branched product and enantioselectivities were only obtained by using lower reaction temperatures. Thus, since the recovered catalytic systems **69**-MK-10_T and **74**-MK-10_T could be reused with no loss of activity or selectivity, we extended the study to the cationic rhodium complex [Rh(cod)(S)-Quinap]BF₄, (**73**), which provides the highest asymmetric induction in the hydroboration of vinylarenes carried out at room temperature [2]. We examined just four consecutive runs in the hydroboration/oxidation of styrene with **73**-MK-10_T (Table 3, entry 4), and from the second consecutive run the activity, regio- and stereoselectivities were constant and comparable to those of the homogeneous version (Table 3, entry 3). However, the catalytic system **73**-MK-10_T seems to need an induction period to reach the maximum values already achieved by its homogeneous counterpart. To clarify this point, we stirred the immobilised catalytic system **73**-MK-

10_T in THF for 2 h. The solid was then filtered and dried under vacuum before we started the first run. Figure 15 shows how the activity, and the regio- and enantioselect

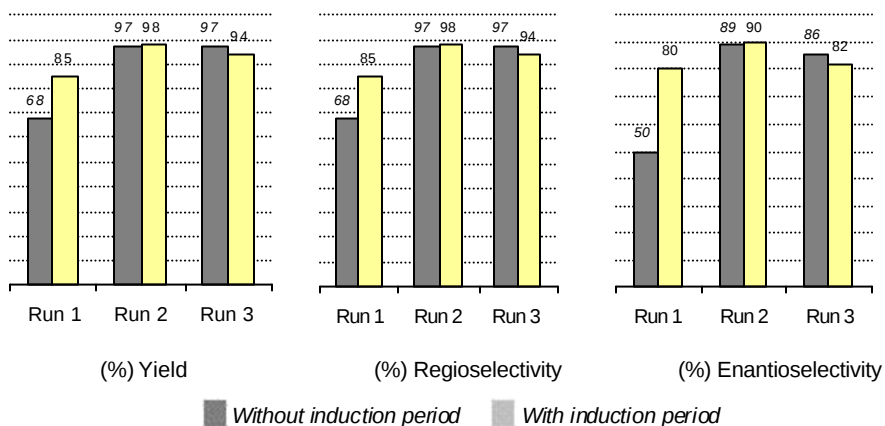


Figure 15

tivity, significantly increased during the first run. It is noteworthy that the filtrates from the induction period of **73**-MK-10_T in THF did not provide any catalysis.

Another interesting catalytic feature of this system is the high degree of stability achieved by the resting state of the catalyst when it is exposed to air.

To illustrate the last point, the solid **73**-MK-10_T was filtered from the reaction products in air between the four consecutive runs. The values for activity, regio- and stereoselectivity were similar after the third consecutive run and these remained constant after recycling (Figures 16 and 17).

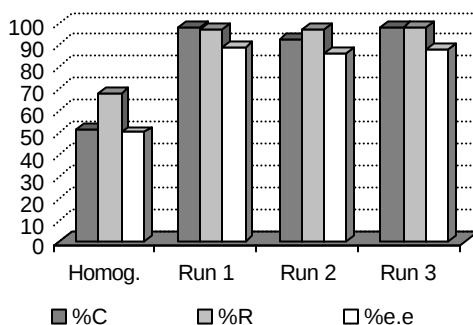


Figure 16

Catalytic activity provided by **73**-MK-10_T filtered under N₂ between the consecutive runs.

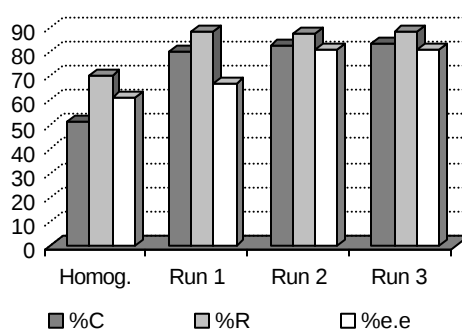


Figure 17

Catalytic activity provided by **73**-MK-10_T filtered under air between the consecutive runs.

It seems that clay is not only an appropriate support for recycling the catalyst, but that it also prevents oxidation or degradation of the catalytic metal species involved in the hydroboration transformations.

Influence of the metal. As has been mentioned in chapter 2, catalytic systems based on rhodium complexes perform better than their iridium analogues in the catalytic hydroboration reaction. In order to observe any effect in the activity and selectivity of the heterogenised iridium complex with respect to its homogeneous analogues, we carried out the hydroboration reaction of styrene with the immobilised complex

[Ir(cod)(R)-Binap]BF₄/MK-10_T, (Table 4). Thus, when [Ir(cod)(R)-Binap]BF₄ (**75**) was used under the same hydroboration conditions as the rhodium system (Table 4, entry 1), conversion was complete but enantioselectivity was almost nil and regioselectivity was only about 30% on 1-phenylethanol. In our ongoing research, we have found that the low enantioselectivity provided by ionic iridium complexes can be improved by immobilising the catalyst precursor onto clays.

Table 4. Asymmetric hydroboration/oxidation of styrene towards (R)-(+)-1-phenylethanol catalysed by the immobilised [Ir(cod)(R)-Binap]BF₄ (**75**).^[a]

Entry	Heterogenised catalytic system	Run (%)	Yield (%)	Branched (%)	e.e. ^[b] (%)
1	75	1	99	30	2
2	75 -MK-10 _T	1	70	17	5
		2	93	31	2

[a] Standard conditions: styrene/catecholborane/Ir complex=1:1.1:0.02. Solvent: THF. T: 25°C. Time: 2 h.; [b] *R* configuration determined by GC with chiral column FS-Cyclodex β-IP, 50 m x 0.25 mm.

This is the case of [Ir(cod)(S,S)-bdpp]PF₆ which efficiently catalyses the hydrogenation of imines such as N-(α-methyl-*p*-methoxybenzylidene)benzylamine with complete conversion but no enantiomeric excess. However, when [Ir(cod)(S,S)-bdpp]PF₆ was immobilised onto MK-10_T, the catalytic system became more enantioselective on re-use, giving values up to 60% of e.e. in a third consecutive run, [7b]. To find a similar effect we immobilised [Ir(cod)(R)-Binap]BF₄ on MK-10_T, and found that after two consecutive runs the activities and selectivities were similar to those provided by the analogous homogeneous systems, (Table 4).

Scope of the recyclable catalytic asymmetric hydroboration reaction. Subsequently, we studied several other vinylarenes, (Figure 18), as substrates for the recyclable catalytic asymmetric reaction, with **73**-MK-10_T as the immobilised catalytic system, following a procedure that was similar to the one described for the hydroboration of styrene.

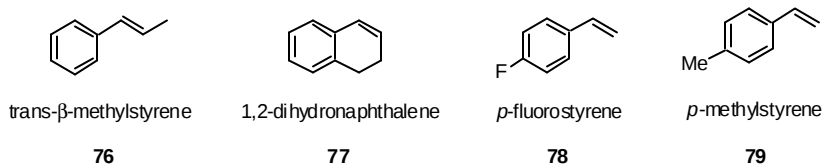


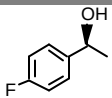
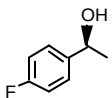
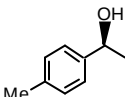
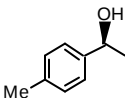
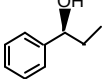
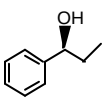
Figure 18

We focused on vinylarene substrates, paying particular attention to those that would highlight how different aryl substituents and β-substitution would affect reactivity and enantioselectivity. In each hydroboration reaction, the immobilised catalytic system was recovered for recycling by filtration. The filtrates were then directly oxidised with H₂O₂ to afford the corresponding alcohol. The results are given in Table 5. When **73**-MK-10_T was used, the electron-deficient substrate *p*-fluorostyrene produced similar activities, regio- and enantioselectivities, after the second consecutive run, to those of the homogeneous system **73** (Table 5, entries 1 and 2).

The asymmetric induction is lower than that of the hydroboration/oxidation of styrene, which agrees with the trends observed with Quinap and other P,N ligands for the hydroboration of styrene reactants with electron-withdrawing substituents [2], [4], [21]. The regio- and stereoselectivities were more satisfactory when electron-releasing aryl substituents were used on the styrene substrate. It is known [2] that electron-rich alkenes are better for achieving maximum stereoselectivity. Therefore, hydroboration/oxidation of the electron-rich *p*-methylstyrene provided an enantiomeric excess of over 90%, both in the homogeneous version and in the heteroenriched version from the third consecutive run, remaining constant on recycling (Table 5, entries 3 and 4).

Table 5 Asymmetric hydroboration/oxidation of vinylarenes towards (S)-(-)-sec-alcohol catalysed by the immobilised [Rh(cod)(S)-Quinap]BF₄ (**73**).^[a]

Entry	Catalytic System	Substrate	(S)-(-)-sec-alcohol	Run	Yield (%)	Branched (%)	e.e. ^[b] (%)
-------	------------------	-----------	---------------------	-----	-----------	--------------	-------------------------

1	73	78		1	97	95	78
2	73-MK-10_T	78		1	38	59	40
				2	83	89	75
				3	92	90	73
				4	82	87	67
3	73	79		1	96	99	91
4	73-MK-10_T	79		1	31	74	70
				2	98	97	89
				3	92	97	86
				4	98	98	88
5	73	77		1	95	99	98
6	73-MK-10_T	77		1	26	98	54
				2	71	95	70
				3	95	98	97
7	73	76		1	92	99	93
8	73-MK-10_T	76		1	5	99	13
				2	66	99	87
				3	66	99	86
				4	64	99	85

[a] Standard conditions: styrene/catecholborane/Rh complex=1:1.1:0.02. Solvent: THF. T: 25 °C. Time: 2 h; [b] S configuration determined by GC with chiral column FS-Cyclodex β-IP, 50 m x 0.25 mm.

For the electron-withdrawing and electron-releasing substrates studied, the supported catalytic system needed an induction period to reproduce the homogeneous values, which may be a little longer for *p*-methylstyrene. The hydroboration/oxidation of 1,2-dihydronaphthalene illustrates the effect of an increase in steric demand around the reaction site. However, enantiomeric excess was highest with the homogeneous catalytic system **73** (e.e= 98%) and the heterogenised system **73-MK-10_T** (e.e= 97%) from the third consecutive run (Table 5, entries 5 and 6). In addition to these results,

we can also see that the induction period required by **73**-MK-10_T in the hydroboration of 1,2-dihydronaphthalene is similar to that of *p*-methylstyrene. A likely explanation is that the more hindered the substrate is, the longer the induction periods need to be. A similar argument can be found in the literature to explain why in the homogeneous hydroboration of vinylarenes with [Rh(cod)(L,L)]X, the higher steric demand of the olefin is more easily accommodated by these less sterically demanding ligands, [21]. Consistently, the hydroboration/oxidation of the β -substituted substrate (E)-propenylbenzene with **73**-MK-10_T gave percentages of the branched product as high as those of its homogeneous counterpart and remained constant on recycling (Table 5, entries 7 and 8). Again, we noted from the catalytic data that increasing the steric demand of the olefin led to a retardation of the reaction.

In all the substrates studied, the catalytic system can be easily separated from the reaction products and recycled for at least the four consecutive runs explored; this demonstrates the scope of this method for recovering and reusing an efficient catalytic system.

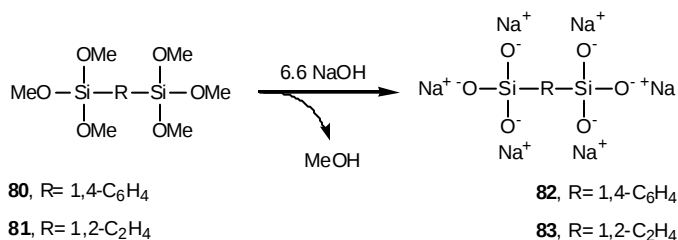
2.2. Comparative study of heterogenised hydroboration between natural bentonites and synthetic organo(bis-silanetriolates) supports

During our search for solids that can be used as supports for immobilising transition metal complexes through ion exchange abilities, we became interested in finding alternative silicate materials. We were particularly attracted by the possibility of using hybrid organic-inorganic materials such as organosilanolates. The literature shows that the simultaneous presence of hydrophilic and hydrophobic interactions can favour the formation of ordered structures, such as organo(bis-silanetriols), which appear as layered structures [10a, b]. This is mainly attributed to the fact that the formation of a strongly hydrogen-bonded network can induce the organisation of hydrophobic organic groups. Similar structural organisation has been found for sodium salts of organo(bis-silanetriolates) [10c]. Therefore, we studied the immobilisation process of complex [Rh(cod)(S)-Quinap]BF₄ (**73**), with sodium phenyl-1,4-bis(silanetriolate) (**82**) and sodium ethyl-1,2-bis(silanetriolate) (**83**), (Scheme 3). As far as

we knew, no previous study had been made on the use of organo(bis-silantriolates) as supports for catalysts. To obtain an overall picture of the influence of supports with ion exchange ability, we also studied two natural bentonites, which differ in surface area and structural features.

2.2.a. Synthesis of hybrid supports: organo(bis-silantriolates)

The sodium phenyl-1,4-bis(silantriolate) (**82**) and sodium ethyl-1,2-bis(silantriolate) (**83**) were prepared by adding a slight excess of NaOH to 1,4-bis(trimethoxysilyl)benzene **80** and to 1,2-bis(trimethoxysilyl)ethane **81**, respectively, (Scheme 3). The compounds **81** and **83** were synthesised for the first time during this thesis, using a methodology that was identical to that for **80** and **82**, as previously reported in the literature [10c].



Scheme 3

The organosilicate compound **83** was identified and characterised by IR, ^1H , ^{13}C and ^{29}Si NMR spectroscopy and X-ray powder diffraction studies. The FTIR spectra (KCl pellets) exhibited adsorption bands centred at 1446, 1139 and 974cm^{-1} attributed to Si-O bond vibration modes, and a broad band centred at 756cm^{-1} probably due to Si-C vibration. Moreover, adsorption bands corresponding to C-H vibrations were detected around 2929 and 2888cm^{-1} . The NMR data was collected in deuterated water, D_2O . ^1H and ^{13}C NMR spectra had the expected resonances for the organic moiety, ($\delta = 0.29\text{ppm}$, (s, 4H) and $\delta = 7.27\text{ppm}$, (s, 2C), respectively). The ^{29}Si NMR spectra showed a sharp resonance at -51.72ppm , in agreement with the chemical shifts already reported for silanetriols [10a, b]. From its X-ray powder diffraction pattern, (Figure 19), the solid was indexed. Si 640b NBS was mixed with the

sample as internal standard. The sample showed the presence of small quantities of Na_2CO_3 whose peaks were well identified. The peak positions were extracted for indexing, with the WinPLOT package [22]. The first 20 lines of the X-ray powder diffraction pattern were indexed with the program TREOR [23] on the basis of a triclinic cell: $a = 6.4108(4) \text{ \AA}$, $b = 11.0738(8) \text{ \AA}$, $c = 6.3107(4) \text{ \AA}$, $\alpha = 103.508(4)^\circ$, $\beta = 91.525(4)^\circ$, $\gamma = 94.033(4)^\circ$, $V = 433.7(5) \text{ \AA}^3$. The reliability of the unit cell and the indexing is indicated by the figures of merit $M_{20} = 59$ and $F_{20} = 101(0.05523, 36)$, [24], [25]. The cell parameters were then refined from the complete powder data with the option Pattern Matching of the program FULLPROF [26].

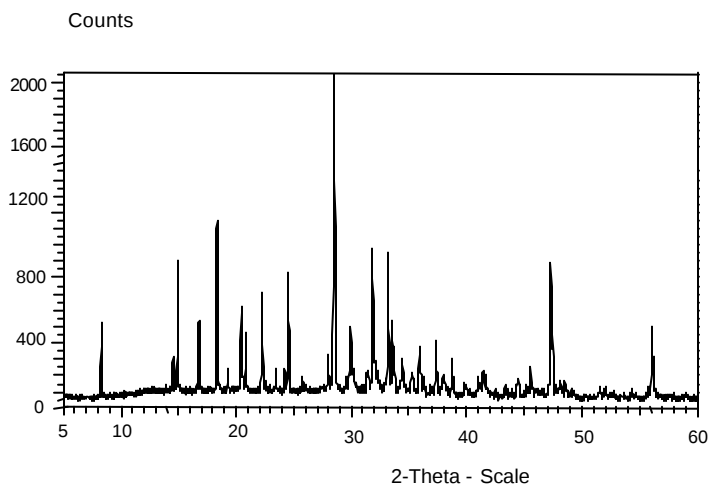


Figure 19

Experimental pattern for the powder-X-ray diffractogram of sodium ethyl-1,2-bis(silantriolate)

2.2.b. Study of the immobilisation process

Section 2.1 of this chapter, showed that natural clays, montmorillonite MK-10 (MK-10) and bentonite (BDH), are viable as solid supports for immobilising transition metal complexes. We have also shown how the differences in crystallinity between both smectite clays can influence the immobilisation pathways observed, because ionic rhodium complexes are mainly immobilised onto MK-10 through adsorptive

forces such as hydrogen bonds [7], but into bentonite through electrostatic forces [5], [6], via previous ion exchange.

In this context, the present section studies the ion exchange immobilisation of ionic complexes with two natural bentonites and two synthetic organo(bis-silanetriolates). The solvent-impregnation method [11] was used to immobilise organometallic complex **73** in both clays: bentonite A and bentonite B. Both bentonites differ from each other in terms of surface area (bentonite A: BET surface area = $53 \text{ m}^2 \text{ g}^{-1}$, bentonite B: BET surface area = $150 \text{ m}^2 \text{ g}^{-1}$), and structural features. The X-ray patterns of the bentonite A and bentonite B supports, (Figure 20), were compared with

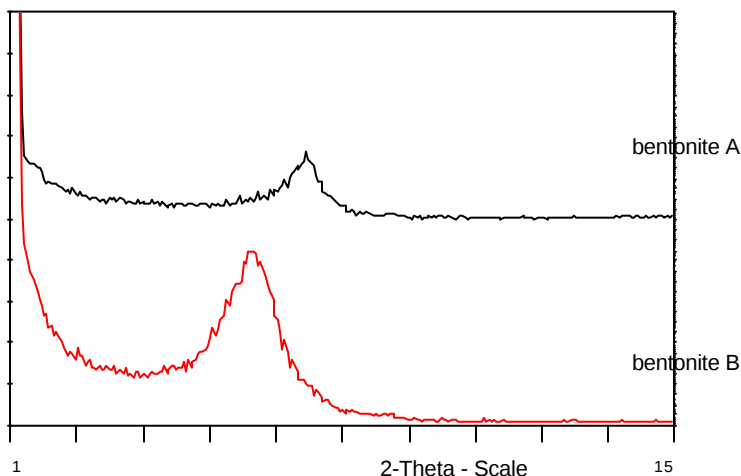


Figure 20

those in the JCPDS-ICDD database. The supports were identified as montmorillonite clay, but the characteristic peaks associated with the (001) reflection were different. In bentonite B the width of this reflection is wider than in bentonite A, and the position is shifted to lower 2-theta values. It is according to an increased basal distance from 12.3 Å in bentonite A to 14.5 Å in bentonite B.

The chemical analyses of bentonite A and B using scanning electron microscopy are compatible with a structure of dioctahedral smectites of theoretical

formula $(H, M^+, M^{2+}_{1/2})_x (Mg_x Al_{2-x})Si_4O_{10} (OH)_2$. However the percentage of Al^{3+} in bentonite B is significantly lower than in bentonite A, (Table 6). This, together with the fact that the percentage of Mg^{2+} is far higher in bentonite B than in A, could indicate a major replacement of Al^{3+} by Mg^{2+} in the octahedral positions of the layer. This substantial substitution may cause an overall increased negative charge on the layer of bentonite B, which requires more hydrated interlayer cations to compensate for the charge, than in the case of bentonite A. This data could be consistent with the increased basal distance observed in bentonite B.

Table 6 Chemical analyses of bentonites and immobilised catalytic systems [Rh(cod)(S)-Quinap]BF₄/bentonites.

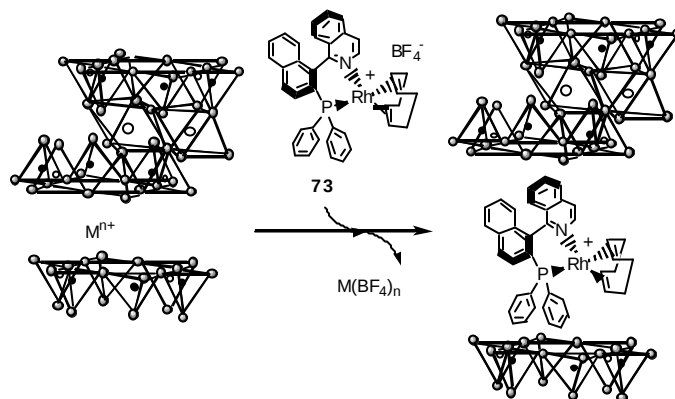
M ³⁺	Bentonite A	73-Bentonite A	Bentonite B	73-Bentonite B
Si	28.7	27.5	25.2	23.0
Al	9.4	9.4	3.2	3.0
O	51.8	48.2	48.2	43.2
Mg	1.7	1.7	14.3	12.4
Na	2.0	2.0	---	---
K	0.8	0.6	0.7	0.8
Ca	1.3	1.1	0.3	0.3
Fe	1.9	2.0	1.5	1.3
Rh	---	0.5	---	0.9

[a] Percentages calculated as (%) from the scanning electron microanalyser analysis.

The bentonites used in the immobilisation procedure were previously dried at 100°C for 24 h to eliminate any adsorbed water. Coloured solutions of the ionic complex in anhydrous dichloromethane were stirred with the solid support for 24h under nitrogen, (scheme 4). The amount of metal complex adsorbed by the clay was determined by gravimetric analysis which measured the difference between the weights of the complex before and after the immobilisation, (Table 7). It should be pointed out that the amount of metal immobilised in bentonite B was approximately twice the amount immobilised in bentonite A, (44.2mg of **73** in 0.5g of bentonite B,

20mg of **73** in 0.5g of bentonite A). This agrees with the fact that the surface area of bentonite B is greater than that of bentonite A. The scanning electron microscopy analyses of **73**-bentonite A and **73**-bentonite B provide the percentages of Rh(I) which agree with the expected amount of Rh(I) in the immobilised metal complex **73** on the solid supports, (Table 6).

The conductimetric analyses made after washing the immobilised catalytic system in both bentonites revealed the presence of ionic species, which indicate that the process that took place was mainly cation-exchange rather than adsorption. As has been seen in section 2.1, we also recorded ^{19}F and ^{31}P NMR spectra in CDCl_3 during the impregnation process. These provided evidence that both bentonites could adsorb the ionic metal complex throughout only the cationic counterpart by ion exchange. We concluded that intensities of the signals of ^{31}P NMR spectra decreased significantly when bentonite A was added, although the intensities of the signals in the ^{19}F NMR spectra did not change throughout the addition of the solid. The reduction of the signals in the ^{31}P spectra during the impregnation process suggests that the cationic counterpart of complex **73** is no longer in solution. In contrast, the F nuclei signals from BF_4^- did not decrease during the impregnation process. This shows that the counteranion might remain mainly in solution, probably as MBF_4 (in which M is the interlamellar metal cation from the bentonites), after exchange with $[\text{Rh}(\text{cod})(\text{S})\text{-Quinap}]^+$. The spectroscopic features for immobilisation with bentonite B were similar. The chemical analyses before and after immobilisation in bentonites show a decrease in the percentages of interlayer cations: K^+ and Ca^{2+} in the case of bentonite A, and Mg^{2+} in the case of bentonite B.



Scheme 4

Table 7. Amounts of immobilised metal complex **73** on the solid supports.

Solid ^[a]	Mmol complex per g solid	Mg complex per 0.5g solid
Bentonite A	0.066	20
Bentonite B	0.110	44.2
Sodium phenyl-1,4-bis(silanetriolate)	0.058	22.6
Sodium ethyl-1,2-bis(silanetriolate)	0.015	5.6

[a] All solids were preheated at 100 °C for 24h; [b] Calculated from the equation [(mg initial complex – mg final complex)/molecular weight complex]/(g solid + g adsorbed complex).

Following the same impregnation procedure mentioned above, we focused our attention at this point on the synthetic organo(bis-silanetriolates) supports. The packing structure of the sodium phenyl-1,4-bis(silanetriolate) is due to the organisation of the phenylene groups, which are all parallel to each other and oriented in the same direction [10c], (Figure 21). Therefore, taking all these structural features into account, we considered about the possibility of using these hybrid salts as supports for ionic metal complexes, through ion exchange. We also explored the influence of the organic pillar, (from phenyl to ethyl), of the organo(bis-silanetriolates) in the immobilisation

ability of the solid and their application in recyclable catalytic asymmetric hydroboration reactions.

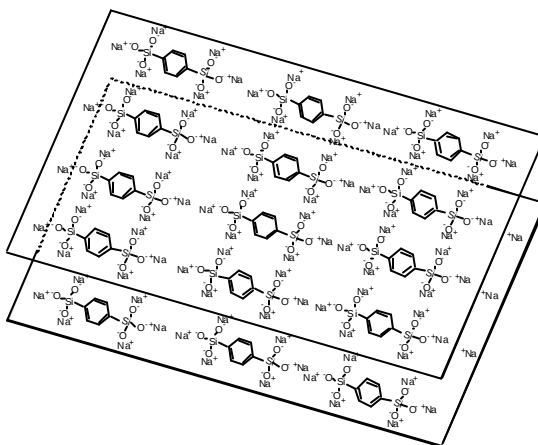
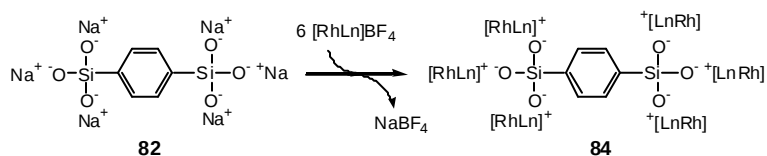


Figure 21

We first looked at the immobilisation process of complex **73** with sodium phenyl-1,4-bis(silanetriolate), (scheme 5).

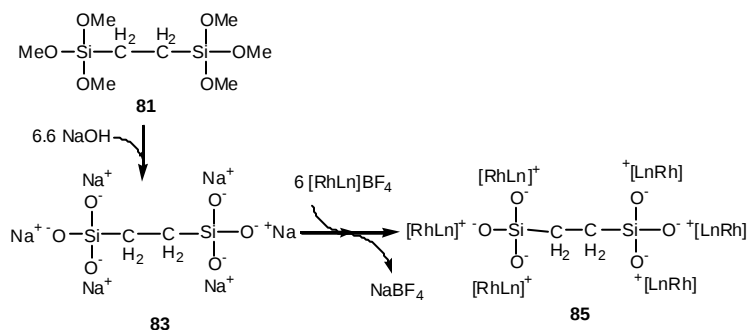


Scheme 5

The amount of metal complex **73** immobilised in sodium phenyl-1,4-bis(silanetriolate) (**82**), was 22.6 mg in 0.5 g of the solid. These data are similar to those of the immobilisation of **73** into bentonite A, (Table 7). After the immobilisation process, the new solid turned yellow, which confirmed the presence of the complex in the support. To determine whether the ion-exchange process had taken place, the immobilised solid was filtered off and washed thoroughly with dichloromethane and

water. Conductimetric analysis and the ^{19}F NMR spectra of the liquid indicated that the counter anion BF_4^- remained in solution, probably as NaBF_4 , after the Na^+ from the solid had been replaced by the cationic complex, as is illustrated in Scheme 5.

In our study of synthetic organo-bis(silantriolates) as supports for immobilising metal complexes, we included a new solid: sodium ethyl-1,2-bis(silantriolate), **83**, (scheme 6). Only 5.63 mg of complex **73** was immobilised in 0.5 g of the sodium ethyl-1,2-bis(silantriolate), (Table 7), during the impregnation procedure. The lack of rigidity in the organic moiety could influence the final organised structure of the solid and, as a result, affect the ion-exchange ability. The different ways of grafting complex **73** to the bentonites and the organo-bis(silantriolates) may lead to differences in their catalytic behaviour when they were used as catalytic systems in the asymmetric hydroboration of vinylarenes.



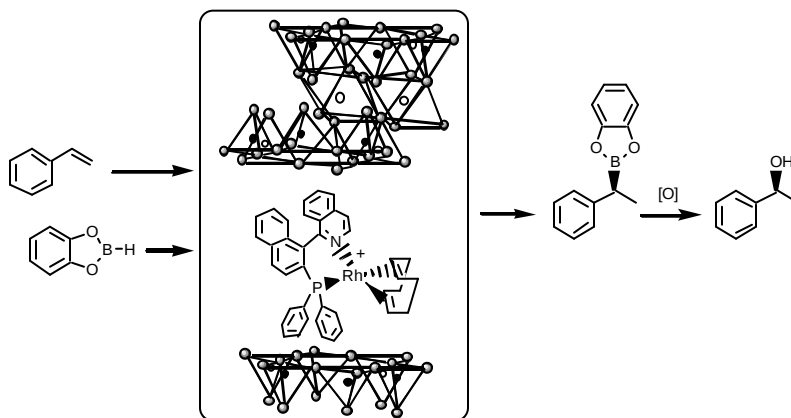
Scheme 6

2.2.c. Study of the heterogenised catalytic hydroboration

The next step was to study the potential of these immobilised systems for the asymmetric hydroboration of vinylarenes. We started by examining the catalytic properties of complex **73** immobilised on both bentonites (bentonite A and B) and the two organo(bis-silantriolates) (**82** and **83**), towards hydroboration/oxidation of styrene as a model substrate. The borane reagent of choice for this study was catecholborane,

because of its efficiency, (Scheme 7). Heterogenised homogenous catalysis makes it possible to separate the chiral alquilborane from the solid catalytic system by simple filtration and then transformed it into its corresponding alcohol via alkaline oxidation, (H_2O_2 , NaOH). We performed the hydroboration of styrene under standard conditions, so that the activity and stability of the supported catalysts could be compared with their homogenous counterparts.

As shown in table 8, the activity and selectivity of complex **73** immobilised in bentonites is much higher than that observed for **73** when it is immobilised in organo(bis-silanetriolates). We examined just four consecutive runs in the hydroboration/oxidation of styrene in all the cases. Only when **73**-bentonite A was used as the catalytic system, was it possible to get values of conversion, regio- and stereoselectivity from the third consecutive run, that were similar to those of the homogeneous system, remaining constant on recycling, (Table 8, entries 1 and 2).



Scheme 7

Leaching of the rhodium complex is not considered because no product was formed when styrene and catecholborane were added to the filtrate of the first run. However, the catalytic system **73**-bentonite A seems to need an induction period to reach the maximum values achieved by its homogeneous counterpart. This induction period seems to be longer than the one required for the heterogenised catalytic system

based on **73** immobilised onto MK-10, (section 2.1.b). This significant difference between the two catalytic systems may be due to the fact that **73** is mainly immobilised in the internal surface of bentonite but mainly grafted on the external surface of montmorillonite K-10.

The closed environment of the metal complex in bentonite A may mean that initially there is a restricted diffusion of the substrate, reactant and product. On the other hand the recyclability of **73**-bentonite B is more irregular than that of **73**-bentonite A, (Table 8, entry 3) and does not achieve the values of conversion, regio- and

Table 8. Asymmetric hydroboration/oxidation of vinylarenes towards (S)-(-)-sec-alcohol catalysed by the immobilised catalytic system [Rh(cod)(S)-Quinap]BF₄ (**73**).^[a]

Entry	Catalytic system	Run	Yield (%)	Branched (%)	e.e. ^[b] (%)
1	73	1	99	95	88
2	73 -Bentonite A	1	33	26	5
		2	93	77	73
		3	93	89	85
		4	90	87	82
3	73 -Bentonite B	1	51	57	18
		2	30	62	37
		3	78	90	71
		4	56	87	60
4	73 - Sodium phenyl-1,4-bis(silantriolate)	1	33	35	3
		2	44	16	1
		3	26	20	27
		4	50	18	20
5	73 - Sodium ethyl-1,2-bis(silantriolate)	1	21	21	1
		2	26	19	1
		3	22	8	3

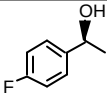
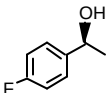
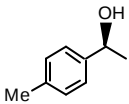
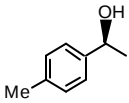
[a] Standard conditions: styrene/catecholborane/Rh complex=1:1.1:0.02. Solvent: THF. T: 25°C. Time: 2 h.; [b] S configuration determined by GC with chiral column FS-Cyclodex β-IP, 50 m x 0.25 mm.

enantioselectivity observed in the homogeneous version. Finally, when **73** is immobilised in the organo(bis-silantriolates), the activity and selectivity observed is very low and is not recovered on recycling, (Table 8, entries 4 and 5). This seems to indicate that the catalytic metal species immobilised in the organo(bis-silantriolates) became less active than when it was immobilised into bentonites.

The scope of the recyclable catalytic asymmetric hydroboration reaction with system **73**-bentonite A, involved an extensive study with several other vinylarenes as substrates. We paid particular attention to those substrates that showed how different aryl substituents and β -substitution can affect reactivity and enantioselectivity. In each hydroboration reaction, the immobilised catalytic system was recovered for recycling by filtration. The filtrates were then directly oxidised with H_2O_2 to afford the corresponding alcohol. The results are given in table 9.

The catalytic system **73**-bentonite A enabled the substrate *p*-fluorostyrene to be converted into its corresponding (S)-(-)-sec-alcohol, and the values of activity, regio- and stereoselectivity, after the second consecutive run, were similar to those observed in the homogenous systems, (Table 9, entries 1 and 2). Although table 9 only shows the four consecutive runs, the catalytic activity remains constant on recycling. When electron-releasing aryl substituents such as *p*-methylstyrene, were used as substrates, the results in terms of stereoselectivity were more satisfactory. In both, the homogenous and the heterogenised version after the second consecutive run, the enantiomeric excess was about 87-91%, (Table 9, entries 3 and 4). On the other hand, the hydroboration/oxidation of the β -substituted substrate (E)-propenylbenzene with **73**-bentonite A, gave percentages of the branched product as high as those of its homogeneous counterpart (99%), but the maximum yield was not higher than 61%. It was probably the increased steric demand of the olefin that delayed the reaction. In all the examples studied, the supported catalytic system seems to need an induction period to reproduce the homogenous values.

Table 9. Asymmetric hydroboration/oxidation of vinylarenes towards (S)-(-)-sec-alcohol catalysed by [Rh(cod)(S)-Quinap]BF₄ (**73**) and **73**-Bentonite A.^[a]

Entry	Substrate	(S)-(-)-sec-alcohol	Run	Yield (%)	Branched (%)	e.e. ^[b] (%)
1 ^[c]	78		1	97	95	78
			1	54	72	61
2 ^[d]	78		2	77	85	74
			3	86	88	83
			4	82	87	83
3 ^[c]	79		1	96	99	91
			1	57	85	87
4 ^[d]	79		2	86	90	87
			3	70	90	85
			4	75	89	86
5 ^[c]	76		1	92	99	93
6 ^[d]	76		1	15	99	7
			2	33	99	61
			3	61	99	83

[a] Standard conditions: styrene/catecholborane/Rh complex=1:1.1:0.02. Solvent: THF. T: 25°C. Time: 2 h; [b] S configuration determined by GC with chiral column FS-Cyclodex β-IP, 50 m x 0.25 mm; [c] catalytic system **73**; [d] catalytic system **73**-bentonite A.

3. Conclusions

A well-defined recyclable catalytic process has been developed in the hydroboration/oxidation reaction of vinylarenes. Immobilised ionic rhodium complexes, $[\text{Rh}(\text{cod})(\text{L},\text{L})]\text{X}$, were prepared by adsorption onto MK-10 τ and by ionic exchange into BDH τ . In addition, the method for preparing the immobilised catalytic system is efficient, uncomplicated and can generally be applied to other ionic complexes.

NMR spectroscopic studies of the resulting solids during the impregnation process suggest that the cationic and anionic counterparts of the complex interact with the MK-10 τ clay probably through weak hydrogen bonding and/or electrostatic forces in a plausible concerted way. The same study also suggested that only the cationic counterpart of the complex is grafted to the bentonite support, probably through electrostatic interactions, and that counteranion remains in solution.

The immobilised rhodium complexes $[\text{Rh}(\text{cod})(\text{L},\text{L})]\text{X}/\text{MK-10}\tau$ exhibits in the catalytic asymmetric hydroboration/oxidation reaction, a comparable activity and selectivity to those of the homogeneous catalyst, irrespective of the nature of the counteranion (when $\text{X} = \text{BF}_4, \text{PF}_6, \text{SO}_3\text{CF}_3$) or ligand (when $(\text{L},\text{L}) = (\text{R})\text{-Binap}, (\text{S},\text{S})\text{-bdpp}, (\text{S})\text{-Quinap}$). The tendency of the BPh_4^- to coordinate to the metal in ionic rhodium complexes can be prevented by immobilising the complex on MK-10 τ , which produces a more active and selective catalytic system than its homogeneous counterpart. In addition, the heterogenised chiral catalyst can be separated from the reaction mixture by simple filtration and reused for several consecutive runs with no loss in activity or selectivity. No leaching of the metal was detected.

The highest activity and selectivity of the heterogenised hydroboration/oxidation reaction of vinylarenes was achieved using the $[\text{Rh}(\text{cod})(\text{S})\text{-Quinap}]\text{BF}_4$ immobilised on predried MK-10 (MK-10 τ), although some induction period is required to reproduce the optimum values of the analogous homogeneous catalytic system.

The catalytic asymmetric hydroboration reaction with supported ionic complexes was efficiently applied to several vinylarenes: *p*-substituted, *b*-substituted and bulky styrenes.

The recovered catalytic system seems to become stable in the absence of excess alkenes and it can be recycled even if the solid is exposed to air when it is manipulated between the consecutive runs.

The reuse and reproducibility of the heterogenised catalytic asymmetric hydroboration/oxidation reaction for a wide number of vinylarenes, makes it viable and practical from both economic and technical perspectives.

The recycling ability of [Rh(cod)(S)-Quinap]BF₄/bentonite A towards hydroboration/oxidation of vinylarenes is similar to that of the catalytic system immobilised onto MK-10 although the grafting of the metal complex seems to be essentially different.

The synthetic organo(bis-silantriolates) were prepared and characterised as new supports for immobilising metal rhodium complexes. However their grafting capacity was lower than that of natural clays for anchoring complex **73**. The [Rh(cod)(S)-Quinap]BF₄, immobilised in both synthetic supports (sodium phenyl-1,4-bis(silantriolate), and sodium ethyl-1,2-bis(silantriolate), were applied to the catalytic asymmetric hydroboration reaction. The activity and selectivity observed were very low and were not recovered on recycling.

4. Experimental Section

General Comments. All reactions and manipulations 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 on a molecular sieve (0.4 nm Aldrich), and degassed with a nitrogen flow prior to use. The complexes $[M(\mu\text{-Cl})(\text{cod})]_2$ [27], $[M(\text{cod})_2]\text{BF}_4$ [28], [29], $[M(\text{cod})(\text{R})\text{-Binap}]\text{BF}_4$ [30], $[M(\text{cod})(\text{R})\text{-Quinap}]\text{BF}_4$ [2], (where $M=\text{Rh, Ir}$) were prepared as previously reported. They were characterized by elemental analysis, ^1H and ^{31}P NMR, and FTIR spectroscopies. MK-10 was purchased from Fluka and bentonite BDH was purchased as Majorbenton B from AEB Iberica S.A. Predried clays were obtained as follows: clay (5g) was kept in a melting pot in the oven at 100°C for 24 h. Calcined MK-10 (MK-10₄₀₀) was obtained as described below: MK-10 (5 g) was kept in a melting pot in the oven at 400°C for 3h. 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. Solid-state ^{31}P NMR spectra were recorded at room temperature on a Varian Mercury spectrometer equipped with a 7 mm BB-CP MAS probe at a working frequency of 161.97MHz. The spectra were recorded by using the cross-polarisation pulse sequence at room temperature under magic angle spinning at a spinning rate of 5.5kHz. For the unsupported rhodium complex, the CP MAS ^{31}P NMR spectrum was collected after 200 scans with a recycle delay of 5s. The MAS ^{31}P NMR spectrum of the supported complex was acquired with 1600 scans and a relaxation delay of 5s. The line broadening was set to be at 90Hz for the free complex and 1300 Hz for the supported complex. 85% H_3PO_4 was used 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. The elemental analysis of organometallic complexes was carried out on an Carlo-Erba Microanalyser EA 1108. IR spectra (range 4000-400 cm^{-1}) were recorded on a FTIR MIDAC PROSPECT-IR spectrometer with KBr pellets. Powder X-ray diffraction (XRD) measurements were made using a Siemens D5000 diffractometer (Bagg-Brentano parafofocusing geometry and vertical θ - θ

goniometer) fitted with a curved graphite diffracted-beam monochromator, incident and diffracted-beam Soller slits, a 0.06° receiving slit and scintillation counter as a detector. The patterns were recorded for 2θ angles between 3° and 70° . The data were collected with an angular step of 0.02° at 10s per step and sample rotation. $\text{CuK}\alpha$ radiation was obtained from a copper X-ray tube operated at 40kV and 30mA. XRD analyses of all the samples were performed in thin films. X-ray diffraction was used to determine the basal spacing of the free supports and the supports with the adsorbed complexes. The basal spacing of each sample was calculated from the (001) reflection in its X-ray pattern. This basal spacing was associated with the distance between (001) layers (d_{001}) and was located at angles (2θ) between 5° and 7° . BET surface areas were calculated from nitrogen adsorption isotherms at 77K by using a Micromeritics ASAP 2000 surface analyser and a value of 0.164nm^2 for the cross section of the nitrogen molecule. The conductivity of the filtrates obtained in the immobilisation process was measured with a Crison microCM 2201 conductimeter. The filtrates were first concentrated under vacuum and diluted with 50 ml of dichloromethane. The scanning electron microscopy analyses were made in a JEOL, JSM-640 with an accelerating voltage=15KV and a probe current = $(3\text{-}6)\times 10^{-9}$ A for a representative area ($575 \times 466 \mu\text{m}$) for each sample.

Preparation of the heterogenised complexes. The ionic rhodium complex was immobilised in the following manner. The solid supports (smectite clays or organo(bis-silantriolates)) were added to an organometallic solution prepared with 10ml of deoxygenated dichloromethane and 0.2mmol of the complex under nitrogen. Then, it was stirred for 24h under nitrogen at room temperature. The suspension was filtered off and the solid was washed with dichloromethane and dried under vacuum. The amount of metal complex immobilised on the clay was determined by gravimetric analysis and SEM analysis.

Homogeneous catalytic hydroboration/oxidation of styrene with catecholborane. Vinylarene (2mmol) was added to a solution of catalyst (1 mol%) in THF (2mL) under nitrogen. The solution was stirred for 5 min and freshly distilled catecholborane (2mmol) was then added. The mixture was stirred at ambient temperature for 1h and

then quenched with EtOH (2mL). Work up must be carried out carefully because of the risk of explosion when using peroxides with ether and THF. Afterwards, NaOH (2M, 2mL) and H₂O₂ (2mL) were added and the mixture was stirred for several hours. The reaction mixture was extracted with Et₂O (3x20) and washed (NaOH 2M, H₂O, saturated brine). The organic extracts were dried over MgSO₄, and evaporated under reduced pressure. The products were characterised by NMR and quantification was carried out by gas chromatography.

Heterogenised catalytic hydroboration/oxidation of styrene with catecholborane.

Styrene (2mmol) was added to a suspension of supported catalyst (1 mol% immobilised in 0.5g of solid) in THF (2mL) under nitrogen. The solution was stirred for 5 min and freshly distilled catecholborane (2mmol) was then added. The mixture was stirred at ambient temperature for 2h, using the chemical assembly shown in Figure 22. The solution was filtered off under vacuum and the filtrates were then

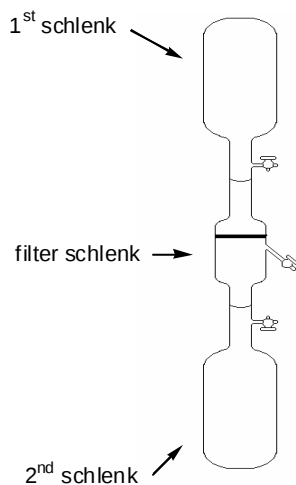
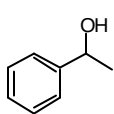


Figure 22

quenched with EtOH (2mL). Work up must be carried out carefully because there is a risk of explosion when using peroxides with ether and THF. The quenched filtrates were treated with NaOH (2M, 2mL) and H₂O₂ (2mL) and the mixture was stirred for

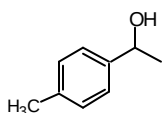
several hours. The mixture was finally extracted into Et₂O, washed (NaOH 2M, H₂O, saturated brine) and dried over MgSO₄. The products were then characterised by NMR and quantification was carried out by gas chromatography. The solid that contained the complex was dried under vacuum for 10 minutes and put into the *schlenk* for another run.

Phenylethanol [3]



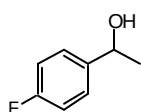
¹H RMN (CDCl₃): δ(ppm)= 7.50-7.20 (m, 5H), 4.55 (q, ³J_{H-H}=6.7Hz, 1H), 1.80(br s, 1H), 1.50 (d, ³J_{H-H}=6.6Hz, 3H).

1-(4-Methylphenyl)etanol [2]



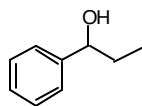
¹H RMN (CDCl₃): δ(ppm)= 7.29 (d, ³J_{H-H}=8.2Hz, 2H), 7.19 (d, ³J_{H-H}=8.2Hz, 2H), 4.86 (q, ³J_{H-H}=6.6Hz, 1H), 2.36 (s, 3H), 1.80(br s, 1H), 1.48 (d, ³J_{H-H}=6.6Hz, 3H).

1-(4-Fluorophenyl)etanol [2]



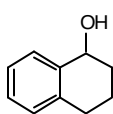
¹H RMN (CDCl₃): δ(ppm)= 7.40-7.10 (m, 4H), 4.86 (q, ³J_{H-H}=6.4Hz, 1H), 1.90 (br s, 1H), 1.48 (d, ³J_{H-H}=6.4Hz, 3H).

1-phenylpropanol [2]



¹H RMN (CDCl₃): δ(ppm)= 7.50-7.20 (m, 5H), 4.55 (q, ³J_{H-H}=6.7Hz, 1H), 2.23 (br s, 1H), 1.90-1.50 (m, 2H), 0.88 (d, ³J_{H-H}=6.7Hz, 3H).

1,2,3,4-Tetrahydro-1-naphthol [2]



^1H RMN (CDCl_3): $\delta(\text{ppm}) = 7.50\text{--}7.10$ (m, 4H), 4.80 (t, $^3J_{\text{H-H}} = 4.3\text{Hz}$, 1H), 3.10–2.70 (m, 2H) 2.10–1.70 (m, 4H).

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