

How To Turn the Catalytic Asymmetric Hydroboration Reaction of Vinylarenes into a Recyclable Process

Anna M. Segarra,^[a] Ramon Guerrero,^[b] Carmen Claver,^[a] and Elena Fernández*^[a]

Abstract: Optically pure rhodium(II) complexes [Rh(cod)(L–L)]X (cod = cyclooctadiene; L–L = (*R*)-2,2'-bis(diphenylphosphino)1-1'-binaphthyl ((*R*)-BINAP), (*S,S*)-2,4-bis(diphenylphosphino)pentane ((*S,S*)-BDPP), 2-diphenylphosphino-1-(1'-isoquinolyl)naphthalene ((*S*)-QUINAP); X = BF₄, PF₆, SO₃CF₃, BPh₄) were immobilised onto smectite clays such as montmorillonite K-10 (MK-10) and bentonite (Na⁺-M). ¹⁹F, ³¹P and ¹¹B NMR experiments recorded in CDCl₃ during the impregnation process provided evidence that

montmorillonite K-10 may immobilise ionic metal complexes throughout the cationic and anionic counterparts. However, when bentonite was used as the solid, only the cationic metal complex was immobilised through cationic exchange while the counteranion remained in solution. When we used these preformed catalytic systems in the hydroboration of prochiral vinylarenes, we

obtained high activities and enantiomeric excess with (*S*)-1-(2-diphenylphosphino-1-naphthyl)isoquinoline-modified rhodium complexes. These activities and selectivities are competitive with the homogeneous counterparts. The significant features of this method are the simple separation and good retention of the active metal in the solid, which allows efficient recycling even on exposure to air.

Keywords: asymmetric catalysis • clays • hydroboration • immobilisation • rhodium

Introduction

The catalytic asymmetric hydroboration reaction has proved to be one of the most convenient reactions in organic synthesis. It provides a way of transforming alkenes into many different types of C*–X and C*–R bonds through the optically enriched organoboron adduct C*–B. The success of the global pathway is mainly due to two steps: 1) the efficient induction of asymmetry in the hydroboration of vinylarenes by the metal complex modified by chiral ligands to obtain C*–B, and 2) the consecutive C*–O,^[1–9] C*–N^[10–12] or C*–C^[13, 14] bond-forming reaction which can be carried out with total retention of stereochemical integrity (Scheme 1). Catecholborane also plays a special role in the catalytic hydroboration reaction. This borane makes the reaction highly effective, probably because of a combination of its electronic properties, which favour the B–H addition, and its steric properties due to its planar configuration when coordinated to a metal.

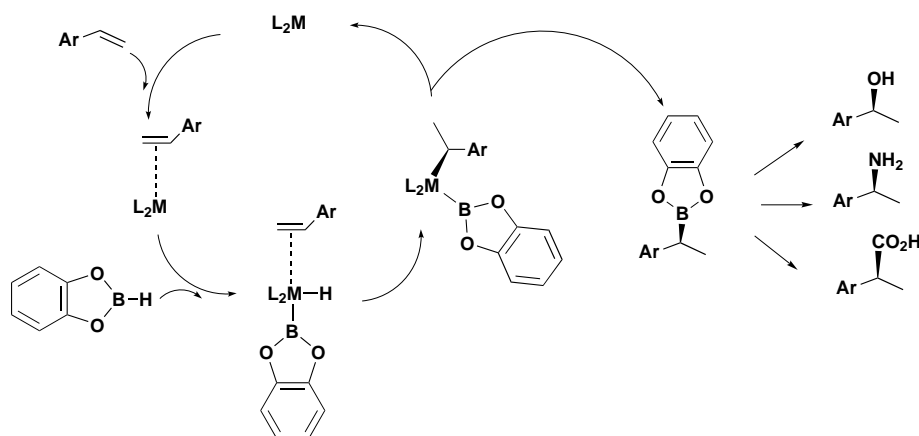
When turnover is complete in the catalytic hydroboration of vinylarenes (to give benzylic boranes) with most rhodium complexes modified with bidentate chiral ligands, the resting state of the catalyst decomposes as a result of its instability in the absence of excess alkene. However, cationic rhodium complexes modified with polycyclic phosphiranes provide a more stable resting state that continues hydroborating after re-addition of alkenes.^[15] However, the catalyst's destruction cannot be avoided during the workup which provides the corresponding alcohols, whether this is done with O₂/H₂O or with the alkaline H₂O₂ medium.^[15]

Therefore, it is desirable to circumvent catalyst destruction by separation before workup to guarantee that the catalytic system remains stable and that it can be reused in new consecutive hydroboration reactions. The advantages of immobilising the homogeneous catalyst on a heterogeneous support are the ease of separation and catalyst recycling combined with similar activities and selectivities of the homogeneous systems. Indeed, all these properties become of great significance for the economic viability of the process, especially when sophisticated chiral ligands are involved.

Common heterogenisation procedures of chiral rhodium complexes involve either their covalent grafting to solid supports such as organic or inorganic solids,^[16] or the dissolution of the precursor in a hydrophilic solvent that is then adsorbed as a thin layer onto a porous support material with a hydrophilic surface^[16] and heteropoly acids as anchor-

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Scheme 1. The catalytic asymmetric hydroboration of vinylarenes by catecholborane.

ing agents.^[17] More recently, a new heterogenisation method based on the three-dimensional entrapment of catalysts by the electrostatic attraction between a polyelectrolyte and an oppositely charged catalyst has been reported.^[18] However, although some of these preformed heterogenised catalytic systems can be efficiently recycled in different enantioselective catalytic transformations, many have the disadvantage that their preparation requires multistep syntheses.

Our studies focus on immobilising catalytic systems in clay structures through absorption or cationic exchange as an easy and clean alternative to heterogenisation.^[19] Indeed, we recently reported that rhodium complexes immobilised in clay montmorillonite K-10 can be highly active, selective and reusable catalysts for the hydroboration reaction of styrene.^[20]

Results and Discussion

Preparation and characterisation of the immobilised catalytic systems:

We carried out the immobilisation process of the organometallic complexes $[\text{Rh}(\text{cod})(\text{L-L})]\text{X}$ (cod = cyclooctadiene; L-L = (*R*)-2,2'-bis(diphenylphosphino)1-1'-binaphthyl ((*R*)-BINAP), (*S,S*)-2,4-bis(diphenylphosphino)pentane ((*S,S*)-BDPP), 2-diphenylphosphino-1-(1'-isoquinolyl)naphthalene ((*S*)-QUINAP); X = BF_4 , PF_6 , SO_3CF_3 , BPh_4) onto the clays montmorillonite K-10 (MK-10) and

bentonite ($\text{Na}^+\text{-M}$), by the previously described solvent-impregnation method (Figure 1).^[21]

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 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 the amount of rhodium

complex $[\text{Rh}(\text{cod})(\text{R})\text{-BINAP}]\text{BF}_4$ (**1**) adsorbed onto the clay is highest when the montmorillonite K-10 was predried for 24 h at 100°C (referred to as MK-10_T) to eliminate any adsorbed water. However, when the montmorillonite K-10 was preheated to 400°C , the resulting calcined solid (MK-10₄₀₀) did not adsorb more rhodium complex than MK-10_T, probably as a result of the loss of interlamellar water resulting in layer collapse. Therefore, the dehydroxylation process during the calcination modifies the residual microporosity and the values of the BET surface area from $221\text{ m}^2\text{ g}^{-1}$ for MK-

Table 1. Amounts of immobilised metal complex **1** on the clays.

Solid ^[a]	Heterogenised catalytic system	mmol complex per g solid ^[b]
MK-10	1 -MK-10	0.055
MK-10 _T	1 -MK-10 _T	0.084
MK-10 ₄₀₀	1 -MK-10 ₄₀₀	0.058
$\text{Na}^+\text{-M}_T$	1 - $\text{Na}^+\text{-M}_T$	0.046
MK-10 _T	2 -MK-10 _T	0.074
MK-10 _T	3 -MK-10 _T	0.085
MK-10 _T	4 -MK-10 _T	0.063
MK-10 _T	5 -MK-10 _T	0.092
MK-10 _T	6 -MK-10 _T	0.093

[a] MK-10: commercial montmorillonite K-10; MK-10_T: preheated at 100°C for 24 h; MK-10₄₀₀: previously calcined at 400°C for 3 h; $\text{Na}^+\text{-M}_T$: commercial bentonite preheated at 100°C for 24 h. [b] Calculated from the equation $[(\text{mg initial complex} - \text{mg final complex})/\text{molecular weight complex}]/(\text{g solid} + \text{g adsorbed complex})$.

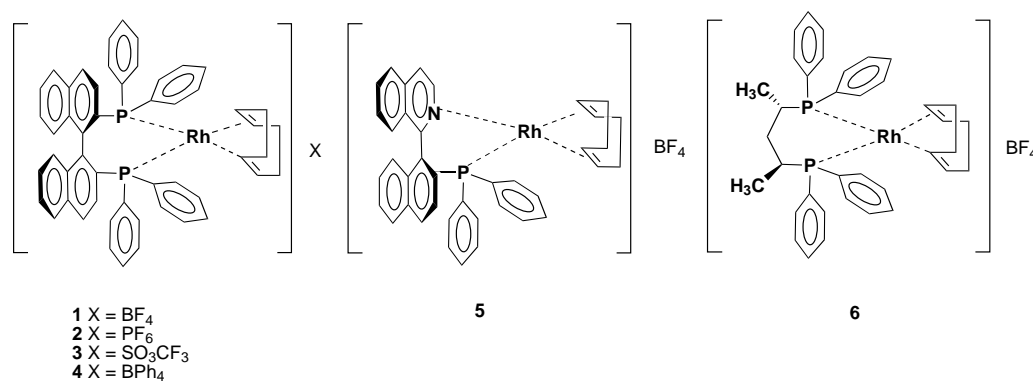


Figure 1. Structures of organometallic complexes used in the immobilisation process.

10_T to $211 \text{ m}^2 \text{ g}^{-1}$ for MK-10₄₀₀.^[22] The percentages of rhodium complexes with other counterions ($X = \text{PF}_6, \text{SO}_3\text{CF}_3, \text{BPh}_4$) adsorbed onto MK-10_T were very similar (Table 1). Conductimetric and ^{19}F and ^{11}B NMR analyses of the liquid filtrate after the impregnation process indicated that the counterions ($\text{BF}_4, \text{PF}_6, \text{SO}_3\text{CF}_3, \text{BPh}_4$) were not present in the filtrates, presumably because they were adsorbed on the support. There was a noticeable difference when preheated bentonite ($\text{Na}^+\text{-M}_T$) was used as support. Following the same impregnation procedure, the amount of metal complex adsorbed was only $0.046 \text{ mmol } \mathbf{1} \text{ g}^{-1}$ clay. This data is in agreement with the lower surface area of $\text{Na}^+\text{-M}_T$ ($53 \text{ m}^2 \text{ g}^{-1}$) relative to MK-10_T. It is known that although both montmorillonite K-10 and bentonite are the same montmorillonite clay material, they show significant differences in crystallinity.^[23] In fact MK-10 is prepared from $\text{Na}^+\text{-M}$ by acid treatment, which partially destroys the bentonite layer structure to produce a disordered and increased surface area. Also, conductimetric analyses of the washings from the immobilised catalytic system in bentonite revealed the presence of ionic species, which indicate that a mainly cation-exchange process took place rather than adsorption. The powder X-ray diffraction data therefore showed an insignificant shift in the (001) diffraction line on the diffractogram between MK-10_T and $\mathbf{1}\text{-MK-10}_T$, but an increased basal distance from 11.8 \AA in $\text{Na}^+\text{-M}_T$ to 16 \AA in $\mathbf{1}\text{-Na}^+\text{-M}_T$.

We recorded ^{19}F , ^{31}P and ^{11}B NMR spectra in CDCl_3 during the impregnation process. These provided evidence that MK-10_T could adsorb ionic metal complexes throughout the cationic and anionic counterparts. In contrast, the immobilisation of the same complexes into bentonite occurred throughout only the cationic counterpart by ion exchange. The ^{19}F NMR spectra of $\mathbf{1}$ had two singlets at $\delta = -154.2$ and -154.3 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 2b), while the ^{31}P spectra had a doublet at $\delta = 26.2 \text{ ppm}$ ($J_{\text{P-Rh}} = 145.4 \text{ Hz}$) (Figure 2a). The intensity of these signals decreases significantly in the ^{19}F and ^{31}P NMR locked spectra of a slurry in CDCl_3 when MK-10_T is added little by little to complex $\mathbf{1}$ (Figure 3). This is because the concentration of $\mathbf{1}$ 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

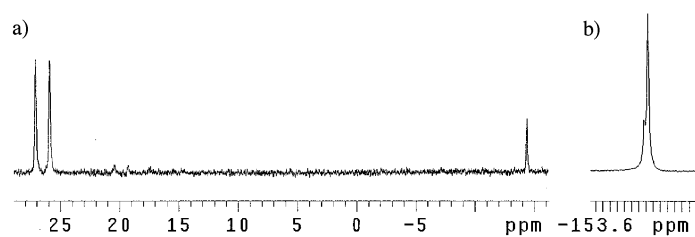


Figure 2. a) ^{31}P NMR spectrum of 20 mg of $\mathbf{1}$ in CDCl_3 + 10 mg of BINAP; b) ^{19}F NMR spectrum of 20 mg of $\mathbf{1}$ in CDCl_3 .

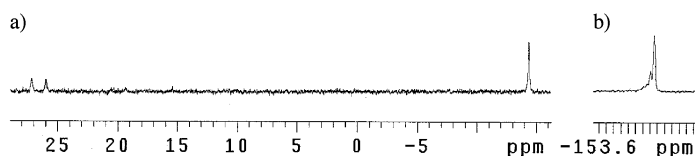
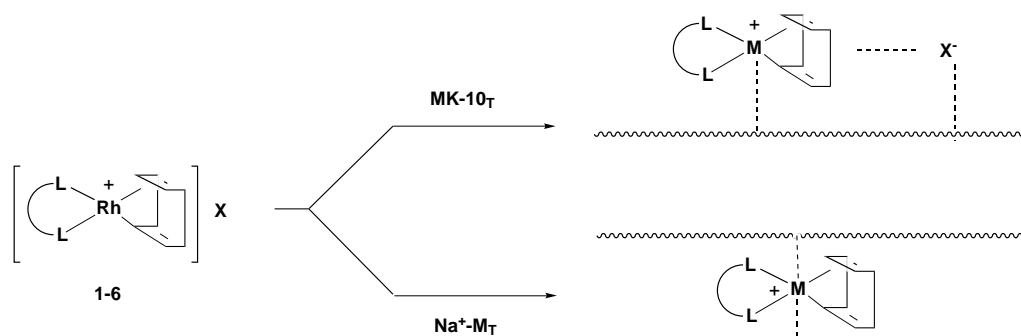


Figure 3. a) ^{31}P NMR spectrum of 20 mg of $\mathbf{1}$ in CDCl_3 + 10 mg of BINAP + 100 mg of MK-10_T; b) ^{19}F NMR spectrum of 20 mg of $\mathbf{1}$ in CDCl_3 + 100 mg of MK-10_T.

addition of an inert reactant such as BINAP (10 mg). Figure 2a and Figure 3a show that after the consecutive addition of MK-10_T, the intensity of the doublet ($\delta(^{31}\text{P}) = 26.4 \text{ ppm}$) due to P nuclei from the coordinated BINAP ligand decreases significantly in comparison with the singlet due to free BINAP ligand ($\delta(^{31}\text{P}) = -14.6 \text{ ppm}$). This is in agreement with the fact that complex $\mathbf{1}$ is being immobilised onto MK-10_T.

Since both nuclei (F and P) were affected in the immobilisation process, we may suggest that the two ionic parts of the metal complex may interact with montmorillonite K-10 through weak forces such as electrostatic and/or hydrogen-bonding interactions (Scheme 2). 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 of different types of silica and the oxygen atom of sulfonate groups from phosphine ligands contained in the zwitterionic rhodium(II) complexes^[24, 25] or from triflate counteranions of cationic Ru^{II} ^[26] and Rh^{I} ^[25, 27] complexes. Unfortunately, as the level of loading of the immobilised complexes was low, we could not confirm the presence of hydrogen bonding by IR spectroscopy. Therefore, taking into



Scheme 2. Schematic representation of the proposed interactions between the metal complexes $\mathbf{1}\text{--}\mathbf{6}$ and montmorillonite K-10 and bentonite on immobilisation.

account the lack of supporting experimental data, we can only suggest that the nature of the interactions between the solid and complex **1** could be due to weak forces such as electrostatic and/or hydrogen bonding.

The MAS ^{31}P NMR spectrum of the grafted complex **1**-MK-10_T is shown in Figure 4b and consists on a broad signal centred at $\delta = 30$ ppm. The CP MAS ^{31}P NMR spectrum of the unsupported complex **1** has a double doublet centred at $\delta = 28$ ppm (Figure 4a). Comparison of the two solid-state NMR spectra suggests that they are substantially similar and thus consistent with the immobilisation of the complex onto montmorillonite K-10.

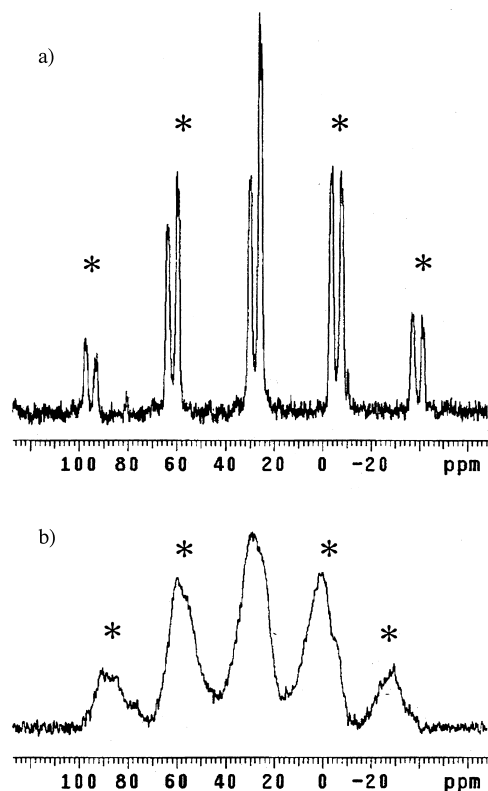


Figure 4. a) CP MAS ^{31}P NMR spectrum of $[\text{Rh}(\text{cod})(R)\text{-BINAP}]\text{BF}_4$; b) MAS ^{31}P NMR spectrum of $[\text{Rh}(\text{cod})(R)\text{-BINAP}]\text{BF}_4\text{-MK-10}_T$. Spinning side bands are denoted by asterisks.

Similar spectroscopic features have been observed during the immobilisation of $[\text{Rh}(\text{cod})(R)\text{-BINAP}]\text{PF}_6$ (**2**), $[\text{Rh}(\text{cod})(R)\text{-BINAP}]\text{SO}_3\text{CF}_3$ (**3**) and $[\text{Rh}(\text{cod})(R)\text{-BINAP}]\text{BPh}_4$ (**4**) onto MK-10_T. With **2–4**, the intensity of the signals decreased significantly on the ^{19}F , ^{31}P and ^{11}B NMR locked spectra of the slurry obtained by consecutively adding MK-10_T to a CDCl_3 solution of the complexes. It is noteworthy that the counteranion BPh_4 is also adsorbed onto MK-10_T 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_T to a solution of complex **4** (Figure 5c 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 ($\text{BAR}_F = \text{B}[\text{C}_6\text{H}_3(\text{CF}_3)_2\text{-3,5}]_4$) as counteranion.^[27]

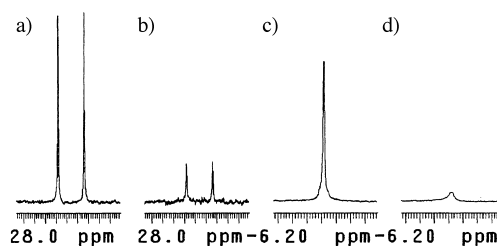


Figure 5. ^{31}P NMR spectrum of a) 20 mg of **4** in CDCl_3 ; b) slurry of a) + 125 mg of MK-10_T. ^{11}B NMR spectrum of c) 20 mg of **4** in CDCl_3 ; d) slurry of c) + 125 mg of MK-10_T.

A remarkable difference was observed between the ^{19}F and ^{31}P NMR experiments carried out during the immobilisation process of **1** into $\text{Na}^+\text{-M}_T$. While the intensities of the signals of ^{31}P NMR spectra decrease significantly when $\text{Na}^+\text{-M}_T$ is added (Figure 6c and d), the intensities of the signals in the ^{19}F NMR spectra did not change throughout the addition (Figure 6a and b). The reduction of the signals in the ^{31}P spectra

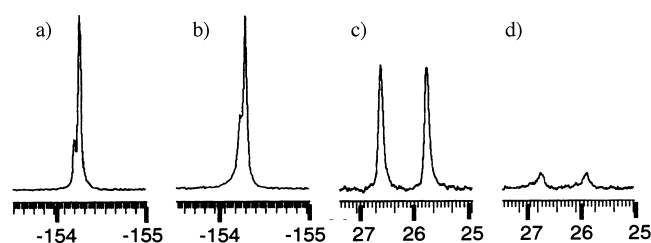


Figure 6. ^{19}F NMR spectrum of a) 20 mg of **1** in CDCl_3 ; b) slurry of a) + 125 mg of $\text{Na}^+\text{-M}_T$. ^{31}P NMR spectrum of c) 20 mg of **1** in CDCl_3 ; d) slurry of c) + 125 mg of $\text{Na}^+\text{-M}_T$.

during the impregnation process suggests that the cationic counterpart of complex **1** 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 [in which M is the interlamellar metal cation from $\text{Na}^+\text{-M}_T$ (Na^+)], which could exchange with $[\text{Rh}(\text{cod})(R)\text{-BINAP}]^+$ (Scheme 2).

In conclusion, the mechanisms for grafting the ionic complexes to MK-10_T and $\text{Na}^+\text{-M}_T$ are different. In the first case, we suggest that the kind of interaction between the counteranion and counteranion to MK-10_T could be due to weak forces, 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 entrapped on the clays imply that there will be differences in the activities and selectivities when they are used as catalytic systems in the asymmetric hydroboration of vinylarenes.

Catalytic asymmetric hydroboration reaction of styrene with the rhodium-immobilised systems: We studied the potential of the immobilised systems in the asymmetric hydroboration

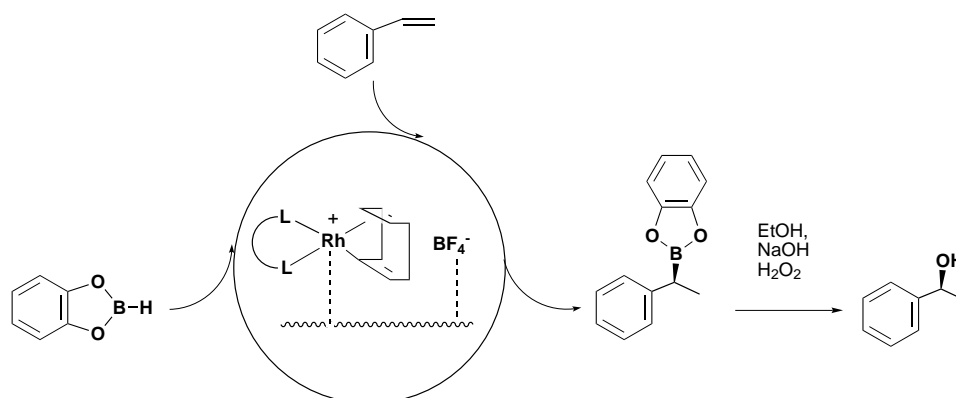
of vinylarenes. We started by examining the catalytic properties of the model rhodium complex $[\text{Rh}(\text{cod})(R)\text{-}(\text{BINAP})]\text{BF}_4$ (**1**) adsorbed on commercial montmorillonite MK-10. In the homogeneous hydroboration/oxidation of vinylarenes, the catalyst precursor **1** provides high yields and regioselectivities for 1-phenylethanol derivatives, but with only moderate enantiomeric excesses (Table 2, entry 1).^[2] This behaviour justifies our choice of this catalytic system, since it may reveal any increase^[17, 19c] 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 $[\text{Rh}(\text{cod})(R)\text{-}(\text{BINAP})]\text{BF}_4$.^[a]

Entry	Catalytic System	Run [%]	Yield [%]	Branched [%]	<i>ee</i> ^[b]
1	1	1	92	99	57
2	1 -MK-10	1	41	92	47
3	1 -MK-10 _T	1	96	97	55
		2	99	97	60
4	1 -Na ⁺ -M _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 B-IP, 50 m × 0.25 mm.

Once the solid-supported catalyst was prepared, it was tested for a) activity, b) regioselectivity, c) enantioselectivity, e) resistance to degradation and f) reusability in the hydroboration/oxidation of the model substrate styrene (Scheme 3). To compare the 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 shown in Table 2, the activity and selectivity of catalyst **1**-MK-10 were 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 may have favoured the degradation of catecholborane and/or the transition metal complex. ¹¹B NMR experiments carried out on MK-10 and catecholborane over the time scale of the catalytic experiment showed that the doublet at $\delta(^{11}\text{B}) = 26.5$ ppm from catecholborane de-



Scheme 3. The hydroboration/oxidation of styrene with the solid-supported catalyst.

creases in intensity as a new broad signal emerges at $\delta(^{11}\text{B}) = 20$ ppm, which can be attributed to the catecholboronate acid formed. However, when the montmorillonite was heated to at least 100 °C before the immobilization of **1**, the activity and selectivity of the resulting supported catalytic system **1**-MK-10_T were similar to those of the homogeneous system. The supported catalyst was removed by filtration under inert atmosphere and hydroboration/recycling repeated without loss of activity or selectivity (Table 2, entry 3). 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. We found significant differences in the hydroboration/oxidation of styrene when we prepared the supported catalytic system from the preheated clay bentonite Na⁺-M_T and complex **1** (Table 2, entry 4). The closed environment of complex **1** immobilised mainly in the internal surface of the bentonite may be different to that of complex **1** 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 is slightly improved in the second consecutive run.

The MAS ³¹P NMR spectrum of the solid **1**-MK-10_T recovered after two consecutive runs has a broad signal centred at 30 ppm (Figure 7). If compared with Figure 4a and b, this is consistent with the permanence of complex **1** or a closed BINAP-Rh complex involved in the reaction, which is immobilised onto the MK-10_T.

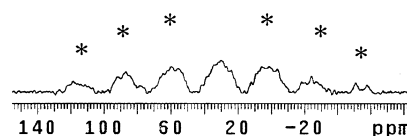


Figure 7. MAS ³¹P NMR spectrum of **1**-MK-10_T after two consecutive runs. Spinning side bands are denoted by asterisks.

Influence of the counteranion: In an attempt to rationalise the catalytic activity exhibited by the supported rhodium complex **1**-MK-10_T, we decided to extend our study to a wider variety of cationic rhodium complexes with different counteranions, such as $[\text{Rh}(\text{cod})(R)\text{-}(\text{BINAP})]\text{X}$ ($\text{X} = \text{PF}_6, \text{SO}_3\text{CF}_3$ and BPh_4) (Figure 8). We therefore immobilised complexes **2**–**4** onto

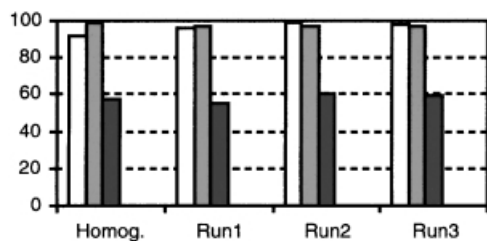


Figure 8. Catalytic activity provided by $[\text{Rh}(\text{cod})(R)\text{-BINAP}]\text{BF}_4$ in the homogeneous and heterogenised hydroboration of styrene (from left to right: % yield, % branched, % ee)

MK-10_T following the same impregnation procedure described above.

The immobilised complex **3** was found to provide the same activity and selectivity as the unsupported complex **3**. It also provided recoverability for at least three consecutive runs in the hydroboration/oxidation of styrene, which was used as the test substrate (Figure 9). Additional insight into a slight

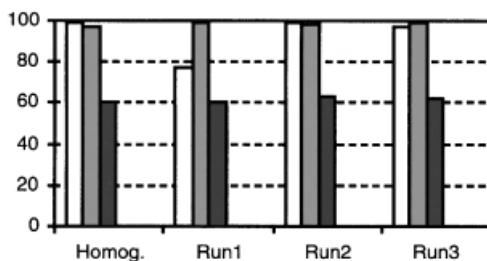


Figure 9. Catalytic activity provided by $[\text{Rh}(\text{cod})(R)\text{-BINAP}]\text{SO}_3\text{CF}_3$ in the homogeneous and heterogenised hydroboration of styrene (from left to right: % yield, % branched, % ee)

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 sulfonates induces enhancements in asymmetric catalysts.^[28] The recyclability of the immobilised catalytic system **2-MK-10_T** is also demonstrated (Figure 10), although selectivity decreased

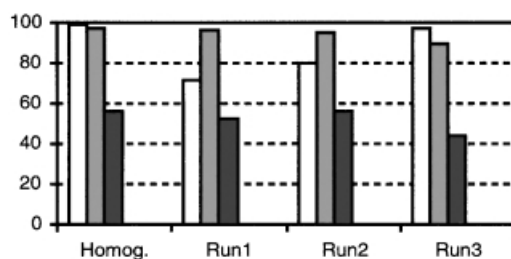


Figure 10. Catalytic activity provided by $[\text{Rh}(\text{cod})(R)\text{-BINAP}]\text{PF}_6$ in the homogeneous and heterogenised hydroboration of styrene (from left to right: % yield, % branched, % ee)

slightly after the third consecutive run. The drop in regio- and enantioselectivities with this system may be due to the less stable immobilised catalytic system 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.^[19a] Even more

striking were the enhanced regio- and enantioselectivities provided by the immobilised catalytic system **4-MK-10_T** relative to its homogeneous counterpart (Figure 11). The proven tendency of BPh_4 to form π complexes and tight ion

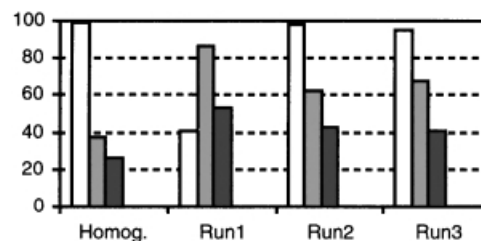


Figure 11. Catalytic activity provided by $[\text{Rh}(\text{cod})(R)\text{-BINAP}]\text{BPh}_4$ in the homogeneous and heterogenised hydroboration of styrene (from left to right: % yield, % branched, % ee)

pairs^[29] might be the cause of the low regio- and enantioselectivities provided by the homogeneous catalytic system **4**. Immobilisation of both the cationic and anionic counterparts of **4** onto montmorillonite K-10 seems to be beneficial for the hydroboration reactions, probably because the counteranion is prevented from coordinating to the metal.^[30] However, although the regio- and enantioselectivities are higher than with the homogeneous version, they do not reach the selectivity of the supported catalytic systems in which $\text{X} = \text{PF}_6$, SO_3CF_3 and BF_4 .

Influence of the ligand: We performed 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.^[31] Two of these conformers are achiral chair conformations with the phenyl rings in an achiral array, and the other two conformers can adopt chiral δ -skew conformations. We wondered whether immobilising a rhodium complex modified with (*S,S*)-BDPP could 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 $[\text{Rh}(\text{cod})(S,S)\text{-BDPP}]\text{BF}_4$ (**6**) and the grafted complex **6-MK-10_T**. There was no significant difference between the catalytic behaviour of the homogeneous version and that of the heterogenised version. Activity and regioselectivity of 1-phenylethanol from complex **6** was high, but enantioselectivity was low and was reproduced with **6-MK-10_T** after the second consecutive run (Table 3, entries 1 and 2).

Another 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 diphenylphosho-naphthalene moieties has been replaced. This structural difference in addition with the electronic features of the P–N ligand explain why the asymmetric induction is higher with chiral QUINAP than with chiral BINAP.^[7] Other axially chiral P–N ligands such as PHENAP,^[4] 2-Ph-quinazolinap^[8] and Pyphos^[32] have been developed over the last few years for use in the

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

Entry	Catalytic System	Run	Yield [%]	Branched [%]	<i>ee</i> [%] ^[b]
1	6	1	98	98	20
2	6 -MK-10 _T	1	82	87	14
		2	97	94	19
3	5	1	99	95	88
4	5 -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 B-IP, 50 m × 0.25 mm.

hydroboration of vinylarenes. However, optimised values for regioselectivities of the branched product and enantioselectivities were only obtained by using lower reaction temperatures. Thus, since the recovered catalytic systems **1**-MK-10_T and **6**-MK-10_T could be reused without loss of activity and selectivity, we extended the study to the cationic rhodium complex [Rh(cod)(*S*)-QUINAP]BF₄ (**5**), which provides the highest asymmetric induction in the hydroboration of vinylarenes carried out at room temperature.^[7] We examined just four consecutive runs in the hydroboration/oxidation of styrene with **5**-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 **5**-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 **5**-MK-10_T in THF for 2 h. The solid was then filtered and dried under vacuum before we started the first run. Figures 12, 13 and 14 show how the activity, regio- and enantioselectivity, respectively, significantly increased during the first run. It is noteworthy that the filtrates from the induction period of **5**-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 was exposed to air. To illustrate this, the solid **5**-MK-10_T was filtered from the reaction products in air between the four consecutive runs. Comparable values for activity, regio- and stereoselectivity are obtained from the

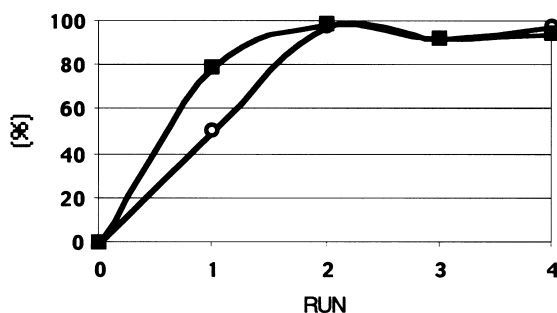


Figure 12. Percentage yield of (*S*)-1-phenylethanol provided by **5**-MK-10_T. With (■) and without (○) induction period.

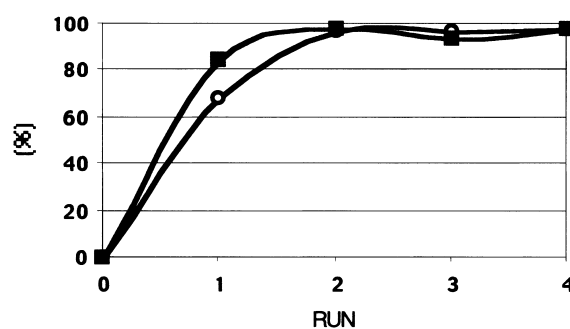


Figure 13. Percentage regioselectivity of (*S*)-1-phenylethanol provided by **5**-MK-10_T. With (■) and without (○) induction period.

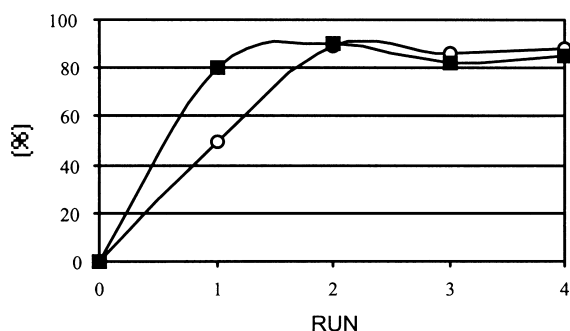


Figure 14. Percentage enantioselectivity of (*S*)-1-phenylethanol provided by **5**-MK-10_T. With (■) and without (○) induction period.

third consecutive run and these remained constant after recycling (Figures 15 and 16). 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.

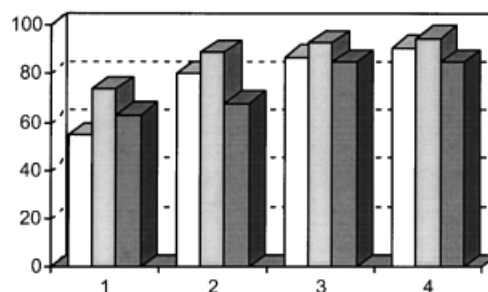


Figure 15. Catalytic activity provided by **5**-MK-10_T filtered under N₂ between the consecutive runs (from left to right: % yield, % branched, % *ee*)

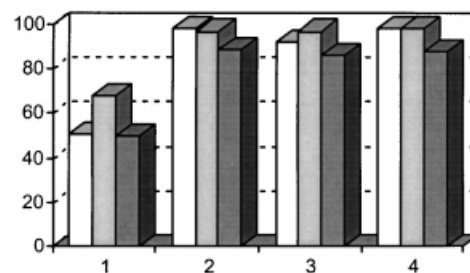


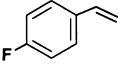
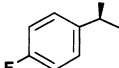
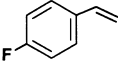
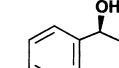
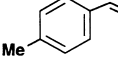
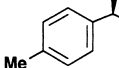
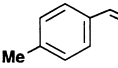
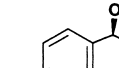
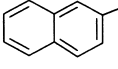
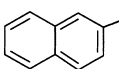
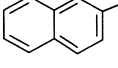
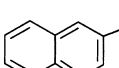
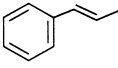
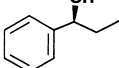
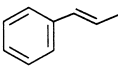
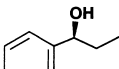
Figure 16. Catalytic activity provided by **5**-MK-10_T filtered under air between the consecutive runs (from left to right: % yield, % branched, % *ee*)

Scope of the recyclable catalytic asymmetric hydroboration reaction: In a subsequent study, we studied several other vinylarenes as substrates for the recyclable catalytic asymmetric reaction with **5**-MK-10_T as the immobilised catalytic system following a similar procedure to that described for the hydroboration of styrene.

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 4. When **5**-MK-10_T was used, the electron-deficient substrate 4-fluorostyrene produced similar activity, regio- and enantioselectivity, from the second consecutive run, to those of the homogeneous system **5** (Table 4, entries 1 and 2). A lower asymmetric induction is obtained in comparison with 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.^[7, 8, 32] More satisfactory results in terms of regio- and stereoselectivity were obtained by using electron-releasing aryl substituents on the

styrene substrate. It is known^[7] that electron-rich alkenes are better for achieving maximum stereoselectivity. Therefore, hydroboration/oxidation of the electron-rich 4-methylstyrene provided an enantiomeric excess of over 90%, both in the homogeneous version and in the heterogenised version from the third consecutive run, remaining constant on recycling (Table 4, entries 3 and 4). 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 4-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 homogenous catalytic system **5** (*ee* = 98%) and the heterogenised system **5**-MK-10_T (*ee* = 97%) from the third consecutive run (Table 4, entries 5 and 6). In addition to these results, we can also see that the induction period required by **5**-MK-10_T in the hydroboration of 1,2-dihydronaphthalene is similar to that of 4-methylstyrene. A likely explanation is that the more hindered the substrate, the longer the induction period needed. A similar argument can be found in the literature to explain why in the homogenous hydroboration of vinylarenes with [Rh(cod)(L–L)]X, the higher steric demand of the olefin is more easily accommodated by these less

Table 4. Asymmetric hydroboration/oxidation of vinylarenes towards (*S*)-(-)-*sec*-alcohol catalysed by the immobilised [Rh(cod)(*S*)-QUINAP]BF₄.^[a]

Entry system	Catalytic	Substrate	(<i>S</i>)-(-)- <i>sec</i> -	Run alcohol	Yield [%]	Branched [%]	<i>ee</i> [%] ^[b]
1	5			1	97	95	78
2	5 -MK-10 _T			1	38	59	40
				2	83	89	75
				3	92	90	73
				4	82	87	67
3	5			1	96	99	91
4	5 -MK-10 _T			1	31	74	70
				2	98	97	89
				3	92	97	86
				4	98	98	88
5	5			1	95	99	98
6	5 -MK-10 _T			1	26	98	54
				2	71	95	70
				3	95	98	97
7	5			1	92	99	93
8	5 -MK-10 _T			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 B-IP, 50 m × 0.25 mm.

sterically demanding ligands.^[8] Consistently, the hydroboration/oxidation of the β -substituted substrate (*E*)-propenylbenzene with 5-MK-10_T gave percentages of the branched product as high as those of its homogeneous counterpart (99%), but the maximum yield was only 64–66%, which remained constant on recycling (Table 4, entries 7 and 8). Again, we noted that increasing the steric demand of the olefin led to a retardation of the reaction as observed from the yields.

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.

Conclusion

To achieve a well-defined catalytic process, the challenge is to develop recyclable catalysts that guarantee the expected activity and selectivity for a reasonable number of consecutive runs. We have managed to fulfil this goal in the hydroboration/oxidation reaction of vinylarenes by preparing immobilised ionic rhodium complexes by adsorption onto montmorillonite K-10 and by ionic exchange into bentonite. The method for preparing the supported catalytic systems is simple, efficient and can generally be applied to other ionic complexes. Improved characterisation of the resulting solids during the impregnation process led us to suggest that the two ionic counterparts of the complex interact with the clay montmorillonite K-10 probably through weak hydrogen-bonded and/or electrostatic forces in a plausible concerted way. The grafted rhodium complexes exhibit a comparable activity and selectivity to those of the free catalyst, irrespective of the counteranion (when X = BF₄, PF₆, SO₃CF₃) or ligand (when L–L = (*R*)-BINAP, (*S,S*)-BDPP, (*S*)-QUINAP). The tendency of the counteranion BPh₄[−] to coordinate to the metal in ionic rhodium complexes can be prevented by immobilising the complex on montmorillonite K-10, which produces a more active and selective catalytic system than its homogeneous counterpart. Activities and regio- and stereoselectivities are highest with [Rh(cod)(*S*)-QUINAP]BF₄ immobilised in predried montmorillonite K-10, although some induction period is required to reproduce the optimum values of the analogue homogeneous catalytic systems. The heterogeneous chiral catalyst can be separated from the reaction mixture by simple filtration. Most of the catalyst is recovered in this way, as leaching of the active species is not detected. Also, the resting state of the catalyst becomes stable in the absence of excess alkene and the catalyst can be recycled even if the solid is exposed to air when it is manipulated between the consecutive runs. The scope of the reaction with the supported ionic rhodium complex was efficiently demonstrated with other *p*-substituted, β -substituted and bulky styrenes. The reuse and reproducibility of the catalytic system in this process makes it viable and practical from economical and technical perspectives.

Experimental Section

General: All reactions and manipulations were conducted with standard vacuum-line techniques under an atmosphere of dry nitrogen. All rhodium organometallic complexes were synthesised by using standard Schlenk techniques. All organic solvents were purified by usual methods, stored over molecular sieves (0.4 nm Aldrich) and degassed with a nitrogen flow before use. The complexes [Rh(μ -Cl)(cod)]₂,^[33] [Rh(cod)₂]X,^[34, 35] [Rh(cod)(*R*)-BINAP]X,^[36] [Rh(cod)(*S,S*)-BDPP]X,^[37] [Rh(cod)(*S*)-QUINAP]X,^[7] (X = BF₄, PF₆, SO₃CF₃, BPh₄) were prepared as previously reported. These complexes were characterised by elemental analysis, ¹H and ³¹P NMR, and FTIR spectroscopies. Montmorillonite K-10 (MK-10) was purchased from Fluka and bentonite Na⁺-M was purchased as Majorbenton B from AEB Iberica S.A. Predried clays were obtained as follows: clay (5 g) in a melting pot was kept in the oven at 100 °C for 24 h. Calcined montmorillonite K-10 was obtained as described below: MK-10 (5 g) in a melting pot was kept in the oven at 400 °C for 4 h. NMR spectra were recorded on a Varian Gemini300 and Mercury400 spectrometer. NMR locked spectra of the slurry in CDCl₃ were carried out by consecutive addition of MK-10_T to a solution of the rhodium complexes. Chemical shifts are reported relative to tetramethylsilane for ¹H and ¹³C, 85% H₃PO₄ for ³¹P and BF₃·OEt₂ for ¹¹B as the external reference. Solid-state ³¹P 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 161.97 MHz. The spectra were recorded by using the cross-polarisation pulse sequence at room temperature under magic angle spinning at a spinning rate of 5.5 kHz. For the unsupported rhodium complex, the CP MAS ³¹P NMR spectrum was collected after 200 scans with a recycle delay of 5 s. The MAS ³¹P NMR spectrum of the supported complex was acquired with 1600 scans and a relaxation delay of 5 s. The line broadening was set to be 90 Hz for the free complex and 1300 Hz for the supported complex. 85% H₃PO₄ 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 FS-Cyclodex B-IP, 50 m × 0.25 mm. Elemental analysis of organometallic complexes was carried out on a Carlo-Erba microanalyser. IR spectra (range 4000–400 cm^{−1}) of KBr discs were recorded on a FTIR Prospect IR of Midac Corporation spectrometer. Powder X-ray diffraction (XRD) patterns of the samples were obtained with a Siemens D5000 diffractometer using nickel-filtered CuK α radiation. XRD analyses of all the samples were performed in thin films. The patterns were recorded for 2 θ angles between 3° and 70°. 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 (2 θ) between 5° and 7°. BET surface areas were calculated from nitrogen adsorption isotherms at 77 K by using a Micromeritics ASAP 2000 surface analyser and a value of 0.164 nm² for the cross section of the nitrogen molecule.

Preparation of the supported complexes: The ionic rhodium and iridium complexes were immobilised in the following manner: dichloromethane solutions (5 mL) of each complex (0.2 mmol) were prepared under nitrogen and added to a suspension of the solid support (MK-10_T and Na⁺-M_T) in deoxygenated dichloromethane (10 mL) and then stirred for 24 h 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.

Homogeneous catalytic hydroboration/oxidation of styrene: Styrene (2 mmol) was added to a solution of catalyst (1 mol%) in THF (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 2 h and then quenched with EtOH (2 mL). Workup must be carried out carefully owing to the risk of explosion when using peroxides with ether and THF. Afterwards, NaOH (2 M, 2 mL) and H₂O₂ (2 mL) were added and the mixture was stirred for several hours. The reaction mixture was extracted into Et₂O, washed with NaOH (2 M), H₂O and saturated brine, dried over MgSO₄, and the products were characterised by chromatography.

Heterogenised catalytic hydroboration/oxidation of styrene: Styrene (2 mmol) was added to a suspension of supported catalyst (1 mol% immobilised in 0.5 g of clay) in THF (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 2 h. The solution was filtered off under vacuum and the filtrates were then quenched with EtOH (2 mL). Workup must be carried out carefully due to the risk of explosion when using peroxides with ether and THF. The quenched filtrates were treated with NaOH (2 M, 2 mL) and H₂O₂ (2 mL) and the mixture was stirred for several hours. The mixture was finally extracted into Et₂O, washed with NaOH (2 M), H₂O and saturated brine and dried over MgSO₄. The products were then characterised by chromatography. The solid that contained the complex was dried under vacuum for 10 min and introduced into the Schlenk for another run.

Acknowledgement

The authors are grateful to the Ministerio de Educación y Tecnología for financial support (reference BQU2001-0656) and the Institut d'Estudis Avançats for grant 2001-IEA34.

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Received: May 16, 2002 [F4096]