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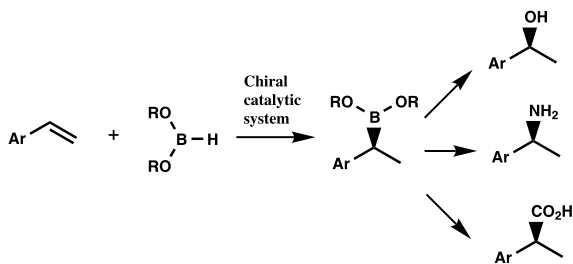
# Efficiency of natural bentonite versus synthetic organo(bis-silantriolates) as supports towards the heterogenisation of asymmetric hydroboration

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**Abstract**—Ionic chiral rhodium complexes can be separated, recovered and reused between consecutive asymmetric catalytic hydroboration reactions of vinylarenes, more efficiently when they are immobilised by electrostatic attraction on clay bentonite than on organo(bis-silantriolates). © 2003 Elsevier Science Ltd. All rights reserved.

A variety of chiral products such as chiral alcohols, chiral amines and chiral homologated compounds, can be successfully prepared by transforming organoboranes into their corresponding functionality.<sup>1–3</sup> Therefore, chiral organoboranes are considered to be interesting organic intermediates in asymmetric synthesis.<sup>4</sup> To date, a reasonably efficient pathway for preparing chiral organoboranes involves hydroboration of unsaturated hydrocarbons.<sup>5</sup> However, the catalytic version has been established as the most appropriate route towards an efficient control of chemo-, regio- and enantioselectivity, using catecholborane as the borane source (Scheme 1).<sup>6</sup>



## Scheme 1.

From the results reported to date, some of the chiral ligands that have induced the highest asymmetry in the rhodium-catalysed hydroboration of vinylarenes are diphosphines,<sup>7</sup> diphosphanes<sup>8</sup> and phosphinamines.<sup>9,10</sup>

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Significantly high are the regio- and enantioselectivity provided by the phosphinamine QUINAP in the hydroboration/oxidation of vinylarenes and  $\beta$ -substituted vinylarenes, working at room temperature.<sup>11</sup> However, the instability of the resting state of the catalyst and the difficulty of separating and recycling the expensive rhodium complexes modified with bidentate chiral ligands, are still serious disadvantages. A recent report has focused on recovering the chiral ligand from the solution through the acid/aqueous extraction of the pyridine moiety of the P,N ligand.<sup>10</sup> However, in addition to the fact that the experimental multistep process eventually reduces the enantiomeric excess of the ligand, the transition metal complex is not recovered. In view of these limitations, we have recently developed a method for separating, recovering and reusing ionic metal complexes modified with chiral ligands from catalytic processes. This method immobilises the catalytic system in clay structures (such as montmorillonite K-10), through adsorptive forces.<sup>12</sup> The resting state of the catalyst also becomes stable and the catalyst can be recycled even if the solid is exposed to air when it is manipulated between consecutive runs. In this context, we wondered about the possible extension of immobilising rhodium complexes into solids, mainly through electrostatic attraction,<sup>13</sup> and their activity and stability on recycling during consecutive hydroboration reactions. This paper compares those solids with ion exchange ability, such as natural bentonites and synthetic organo(bis-silantriolates), that are used as supports for immobilising the enantiomerically pure

rhodium complex [Rh(COD)(S)-QUINAP]BF<sub>4</sub>, **1** (COD = cyclooctadiene, QUINAP = 2-diphenylphosphino-1-(1'-isoquinolyl)naphthalene) and applies them in the hydroboration/oxidation of vinylarenes. As far as we know, there have not been earlier studies related to the use of organo(bis-silantriolates) as supports for catalysts.

We used the solvent-impregnation method to immobilise organometallic complex **1** in two different types of bentonites: bentonite A and bentonite B. The bentonites differ from each other in terms of surface area (bentonite A: BET surface area = 53 m<sup>2</sup> g<sup>-1</sup>, bentonite B: BET surface area = 150 m<sup>2</sup> g<sup>-1</sup>), and structural features. The X-ray patterns of the bentonite A and bentonite B, were compared with 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. This corresponds to an increased basal distance from 12.3 Å in bentonite A to 14.5 Å in bentonite B. Chemical analyses of bentonite A and B were made using scanning electron microscopy (JEOL, JSM-640) for a representative area (575 × 466 μm) for each sample. The chemical analyses of bentonite A and B are compatible with a structure of dioctahedral smectites of theoretical formula (H, M<sup>+</sup>, M<sub>1/2</sub><sup>2+</sup>)<sub>x</sub>(Mg<sub>x</sub>Al<sub>2-x</sub>)Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>. However, the percentage of Al<sup>3+</sup> in bentonite B is significantly lower than in bentonite A (Table 1). This, together with the fact that the percentage of Mg<sup>2+</sup> is far higher in bentonite B than in A, could indicate a major replacement of Al<sup>3+</sup> by Mg<sup>2+</sup> 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 the charge, than in the case of bentonite A. This data could be consistent with the increased basal distance observed in bentonite B. The bentonites used in the immobilisation procedure were previously dried at 100°C for 24 h to eliminate any adsorbed water. Thus, coloured solutions of the ionic complex 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 which measured the difference between the weights of the complex before and after the immobilisation (Table 2). There was a noticeable difference when bentonite B was used as support, because the amount of metal immobilised was approximately twice the amount immobilised in bentonite A (44.2 mg in 0.5 g of bentonite B, 20 mg in 0.5 g of bentonite A). This agrees with the fact that the surface area of bentonite B is higher than that of bentonite A. The scanning electron microscopy analyses of 1-bentonite A and 1-bentonite B provide the percentages of Rh(I) which agree with the expected amount of Rh(I) in the immobilised metal complex **1** on the solid supports (Table 1). Conductimetric analyses of the washings from the immobilised catalytic system in both bentonites revealed the presence of ionic species, which indicate that the process that took place

**Table 1.** Chemical analyses of bentonites and immobilised catalytic systems 1-bentonites<sup>a</sup>

	Bentonite A	1-Bentonite A	Bentonite B	1-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

<sup>a</sup> Percentages calculated as (%) from the scanning electron micro-analyser analysis.

**Table 2.** Amounts of immobilised metal complex **1** on the solid supports

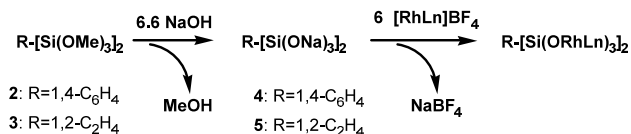
Solid <sup>a</sup>	Mmol complex per g solid <sup>b</sup>	Mg complex per 0.5 g solid
Bentonite A	0.066	20
Bentonite B	0.110	44.2
Sodium phenyl-1,4-bis(silantriolate)	0.058	22.6
Sodium ethyl-1,4-bis(silantriolate)	0.015	5.6

<sup>a</sup> All solids were preheated at 100°C for 24 h.

<sup>b</sup> Calculated from the equation [(mg initial complex – mg final complex)/molecular weight complex]/(g solid + g adsorbed complex).

was mainly cation-exchange rather than adsorption. The chemical analyses before and after immobilisation in bentonites show a decrease in the percentages of interlayer cations: K<sup>+</sup> and Ca<sup>2+</sup> in the case of bentonite A, and Mg<sup>2+</sup> in the case of bentonite B.

In the course of our search for solids that can be used as supports for 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.<sup>14</sup> 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 structure organisation has been found for sodium salts of organo(bis-silantriolates).<sup>15</sup> Therefore, we studied the immobilisation process of complex **1** with sodium phenyl-1,4-bis(silantriolate) and sodium ethyl-1,2-bis(silantriolate), the latter being synthesised and characterised for the first time in this work. Both solids were prepared adding a slight excess of NaOH to 1,4-bis(trimethoxysilyl)benzene<sup>15</sup> **2** and to 1,2-bis(trimethoxysilyl)ethane **3**, respectively (Scheme 2). The sodium ethyl-1,2-bis(silantriolate) was identified



Scheme 2.

and characterised by IR, <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR spectroscopy and X-ray powder diffraction studies. The FTIR spectra (KCl pellets) exhibited adsorption bands centred at 1446, 1139, 974 attributed to Si–O bond vibration modes, and a broad band centred around 756 probably due to Si–C vibration. Moreover adsorption bands corresponding to C–H vibrations were detected around 2929 and 2888 cm<sup>-1</sup>. The NMR data were collected in deuterated water, D<sub>2</sub>O. <sup>1</sup>H and <sup>13</sup>C NMR spectra had the expected resonances for the organic moiety ( $\delta=0.29$  ppm (s, 4H) and  $\delta=7.27$  ppm (s, 2C), respectively). The <sup>29</sup>Si NMR spectra showed a sharp resonance at  $-51.72$  ppm, in agreement with the chemical shifts already reported for silanetriols.<sup>14</sup> From its X-ray powder diffraction pattern, the solid could be indexed. Si 640b NBS was mixed with the sample as internal standard. The extraction of peak positions for indexing was performed with the WinPLOT package.<sup>16</sup> The first 20 lines of the X-ray powder diffraction pattern were indexed with the program TREOR<sup>17</sup> on the basis of a triclinic cell:  $a=6.4108(4)$  Å,  $b=11.0738(8)$  Å,  $c=6.3107(4)$  Å,  $\alpha=103.508(4)^\circ$ ,  $\beta=91.525(4)^\circ$ ,  $\gamma=94.033(4)^\circ$ ,  $V=433.7(5)$  Å<sup>3</sup>. The reliability of the unit cell and the indexing is indicated by the figures of merit  $M_{20}=59$  and  $F_{20}=101(0.05523, 36)$ .<sup>18,19</sup>

Following the same impregnation procedure mentioned above, the amount of metal complex **1** immobilised in sodium phenyl-1,4-bis(silanetriolate) was 22.6 mg in 0.5 g of the solid. These data are comparable to those of

the immobilisation of **1** into bentonite A (Table 2). A remarkable difference was observed in the immobilisation of complex **1** in sodium ethyl-1,2-bis(silanetriolate), because only 5.63 mg of rhodium complex was grafted in 0.5 g of solid (Table 2). The lack of rigidity in the organic moiety of the solid could influence the final organised structure of the solid and, as a result, affect the ion-exchange ability.

The different ways for grafting complex **1** to the bentonites and the organo-bis(silanetriolates) may lead to differences in their catalytic behaviour when they are used as catalytic systems in the asymmetric hydroboration of vinylarenes. We started by examining the catalytic properties of complex **1** immobilised on both bentonites (bentonite A and B) and the two organo-bis(silanetriolates), towards hydroboration/oxidation of styrene as model substrate. Catecholborane was used as the boron source. Heterogenised homogenous catalysis allows the chiral alkylborane to be separated from the solid catalytic system by simple filtration and then transformed into its corresponding alcohol via alkaline oxidation (H<sub>2</sub>O<sub>2</sub>, NaOH). As shown in Table 3, the activity and selectivity of complex **1** immobilised in bentonites is much higher than that observed for **1** when it is immobilised in the organo-bis(silanetriolates). We examined about four consecutive runs in the hydroboration/oxidation of styrene in all the cases. Only when **1**-bentonite A was used as the catalytic system, was it possible to get values of conversion, regio- and stereoselectivity from the third consecutive run, comparable to the homogeneous system, remaining constant on recycling (Table 3, entries 1 and 2). 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 **1**-bentonite A seems to need an induction period to reach the maximum values already achieved by its homogeneous counterpart. To

**Table 3.** Asymmetric hydroboration/oxidation of styrene towards (*S*)-(-)-1-phenylethanol catalysed by the immobilised complex [Rh(COD)(*S*)-QUINAP]BF<sub>4</sub><sup>a</sup>

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

<sup>a</sup> Standard conditions: styrene/catecholborane/Rh complex = 1:1.1:0.02, solvent: THF, T: 25°C, time 2 h.

<sup>b</sup> *S* configuration determined by GC with chiral column FS-Cyclodex B-IP, 50 m×0.25 mm. Values expressed as an average of several reactions.

<sup>c</sup> Ref. 11.

clarify this point, we stirred the immobilised catalytic system in THF for 2 h, and the solid was then filtered and dried before we started the first run. The ee values were >5%, in agreement with the need of an induction period, which seems to be also dependent on the substrate used. On the other hand the recyclability of **1**-bentonite **B** is more irregular than **1**-bentonite **A** (Table 3, entry 3) and does not achieve the values of conversion, regio- and enantioselectivity observed in the homogeneous version. Finally, when **1** is immobilised in the organobis(silantriolates), the activity and selectivity observed is very low and is not recovered on recycling (Table 3, entries 4 and 5). This seems to indicate that the catalytic metal species immobilised in the organo(bis-silantriolates) resulted less active than when was immobilised into bentonites.

The recyclability of **1**-bentonite **A** led us to explore the scope of the asymmetric reaction towards several other vinylarenes. We paid particular attention to those substrates that show how different aryl substituents and  $\beta$ -substitution can affect reactivity and enantioselectivity. The results are given in Table 4. The catalytic system **1**-bentonite **A** enabled the substrate 4-fluorostyrene to be converted into its corresponding (*S*)-(-)-*sec*-alcohol, and the values of activity, regio- and stereoselectivity, from the second consecutive run, were similar to those observed in the homogenous systems (Table 4, entries 1 and 2). Although Table 4 only shows 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 from the second consecutive run, the enantiomeric excess was about 87–91% (Table 4, entries 3 and 4).

On the other hand, the hydroboration/oxidation of the  $\beta$ -substituted substrate (*E*)-propenylbenzene with **1**-bentonite gave percentages on 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. It is worth pointing out that the recycling ability of **1**-bentonite **A** towards hydroboration/oxidation of vinylarenes is similar to that of the catalytic system montmorillonite K-10,<sup>12</sup> although the grafting of the metal complex seems to be essentially different.













### Acknowledgements

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**Table 4.** Asymmetric hydroboration/oxidation of vinylarenes towards (*S*)-(-)-*sec*-alcohol catalysed by **1**-Bentonite **A**<sup>a</sup>

Entry	Substrate	( <i>S</i> )-(-)- <i>sec</i> -alcohol	Run	Yield (%)	Branched (%)	ee (%) <sup>b</sup>
1 <sup>c</sup>			1	97	95	78
2			1	54	72	61
			2	77	85	74
			3	86	88	83
			4	82	87	83
3 <sup>c</sup>			1	96	99	91
4			1	57	85	87
			2	86	90	87
			3	70	90	85
			4	75	89	86
5 <sup>c</sup>			1	92	99	93
6			1	15	99	7
			2	33	99	61
			3	61	99	83

<sup>a</sup>Standard conditions: styrene/cathecholborane/Rh complex = 1:1.1:0.02, solvent: THF, T:25°C, time 2h.

<sup>b</sup>S configuration determined by G.C. with chiral column FS-Cyclodex B-IP, 50 m x 0.25 mm. Values expressed as an average of several reactions.

<sup>c</sup>Ref. 11.

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