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Novel silica-based hybrid materials incorporating binaphthyl units: a chiral matrix effect in heterogeneous asymmetric catalysis

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Abstract

Polysilsesquioxane hybrid materials containing chiral binaphthyl moieties are readily available by coupling (*R*)- or (*S*)-2,2′-dihydroxy-1,1′-binaphthyl (BINOL) with 3-(triethoxysilyl)propyl isocyanate and subsequent hydrolysis polycondensation of the resulting bis-trialkoxysilylated carbamate precursor. Rhodium species were embedded in the chiral hybrid matrix. The catalytic properties of the solids were evaluated in hydride-transfer reduction to prochiral ketones. When the catalytic species were embedded in an entirely chiral network, enantiomeric excesses up to 45% were observed. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Hybrid organic–inorganic solids have been intensively investigated in the last few years.[1–3] Polysilsesquioxanes[4] have proven to be of particular interest since they provide the possibility of the non-reversible and covalent inclusion of a large variety of organic groups into completely amorphous silica frameworks by simple sol–gel processing of trialkoxysilylated organic molecules $(RO)_3Si\text{-}Y\text{-}Si(OR)_3$.[5,6] A large variety of applications have been found to be relevant to organic–inorganic hybrid materials,[2–6] including the preparation of materials for optics or electro-optics,[7] the modification of surface properties[8] as well as the tailoring of new porous materials.[9–12]

Sol–gel derived materials are also of interest in catalysis.[13] The 'heterogenization' of homogeneous catalysts is one of the crucial problems in terms of highly economical and ecological interest. Heterogeneous systems provide a facile catalyst separation and recovery. These aspects are of major importance owing to the purity requirements of chemical products and the high cost

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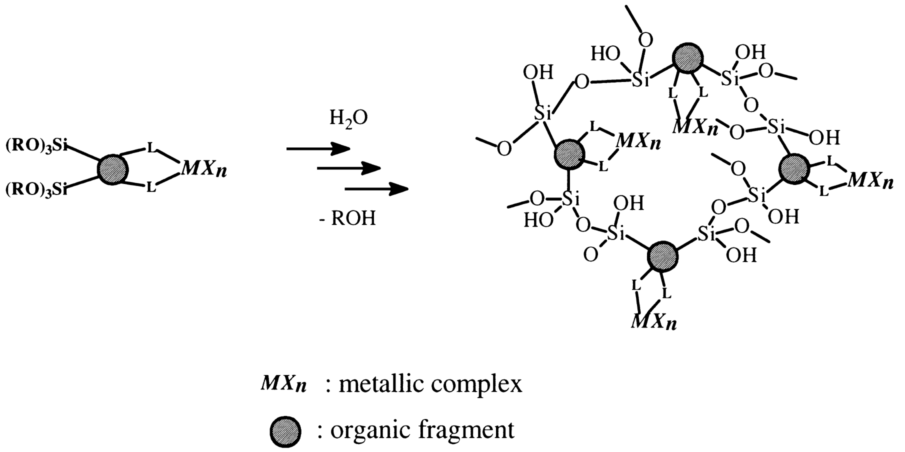
of some transition metals. The sol–gel process has been shown to be suitable for the immobilization of transition metal complexes.[13] Sol–gel hybrid materials are accessible by hydrolysis–polycondensation of organometallic trialkoxysilylated precursors (Scheme 1). They constitute a new class of support for heterogeneous catalysts. A tuning of the solid properties may result from variations in the nature and structure of the organic components. We are currently investigating hybrid sol–gel systems based on chiral organic moieties and their application in molecular recognition and asymmetric catalysis.[14]



Scheme 1. Synthesis of hybrid sol–gel systems incorporating transition metal complexes by hydrolysis polycondensation of silylated organometallic precursor molecules

Recently, we reported the covalent incorporation of silylated rhodium-complexed (1*R*,2*R*)-diaminocyclohexanes in hybrid materials and their use as heterogeneous asymmetric catalysts.[15] In one case, the solid catalyst gave a higher enantioselectivity than that observed with the molecular complex in solution. This may be attributed to an effect of the secondary structure of the chiral hybrid network. With the aim of amplifying this supramolecular effect, we were particularly interested in the incorporation of more rigid chiral organic moieties. We chose 2,2′-dihydroxy-1,1′-binaphthyl (BINOL) as it is widely used as chiral auxiliary in catalytic asymmetric reactions.[16] Ligands derived from enantiomerically pure BINOL exhibit excellent chiral induction in numerous transformations owing to the rigidity and C_2 symmetry of the chiral unit.[17] BINOL-derived ligands were, for example, successfully utilized in asymmetric Diels–Alder reactions,[18,19] Michael reactions,[20,21] ene-reactions,[22,23] epoxidations[24] and nitroaldol reactions.[25]

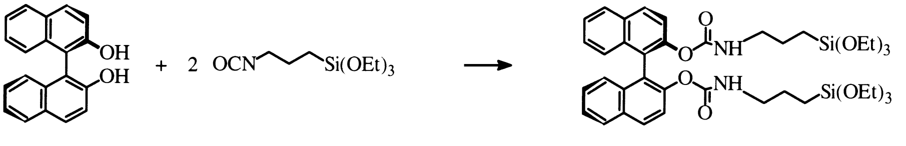
We present here an approach for the elaboration of enantioselective catalysts based on new hybrid solids, in which the enantioselection results not only from the chiral coordination sphere around a transition metal catalyst, but also from a supramolecular effect of an entirely chiral host matrix. We wish to show that chiral hybrids are easily accessible materials which have an interesting potential for organic synthesis and catalysis. Here, we report a facile synthesis of a (*R*)- or (*S*)-BINOL derived bis-carbamate precursors containing hydrolysable $Si(OEt)_3$ groups and their subsequent transformation into hybrid silica gels. Hydrolysis–polycondensation of the chiral precursor in the presence of $[Rh(cod)Cl]_2$ led to hybrid solids containing rhodium species. These materials were evaluated in terms of catalytic activity and enantioselectivity in hydride-transfer reduction of prochiral ketones in order to explore a possible chiral matrix effect.

2. Results and discussion

2.1. Silylation of (R)- and (S)-BINOL and preparation of a chiral xerogel

The trialkoxysilylated precursor **1** was prepared by a coupling reaction between (*R*)- or (*S*)-2,2′-dihydroxybinaphthyl and 3-(triethoxysilyl)propyl isocyanate. The reaction was carried out at room temperature in dichloromethane in the presence of triethylamine. The coupling reaction can easily be monitored by infrared spectroscopy (C=O absorption). Elimination of the solvents afforded the silylated precursors (*R*)- and (*S*)-2,2′-(di-(3-triethoxysilyl)propyl-carbamoyloxy)-1,1′-binaphthyl **1** in excellent yield (Scheme 2) as a colourless and highly viscous liquid.

The hydrolysis–polycondensation of the (*R*)-BINOL derivative was performed under nucleophilic catalysis[26] using ammonium fluoride, since under basic conditions,[1] a cleavage of the carbamate group occurred during gellification. Colourless transparent gels were obtained upon treatment of a tetrahydrofuran solution of the (*R*)-BINOL carbamate **1** with water in the presence of 1 mol% of NH_4F. After curing for 5 days at room temperature, the xerogels **2** were isolated quantitatively as a white powder by washing with tetrahydrofuran and drying in vacuo at 110°C (Scheme 3).



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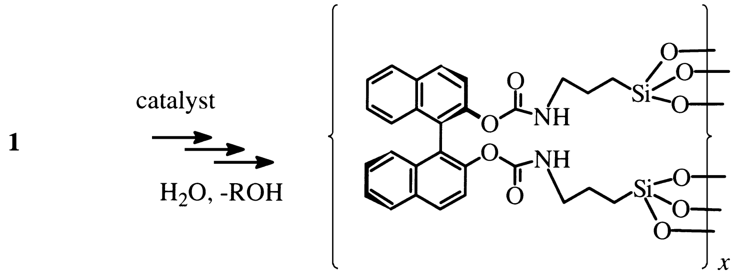
Scheme 2. Synthesis of the bis-carbamate BINOL precursor (*R*)-2,2′-(di-(3-triethoxysilyl)propyl-carbamoyloxy)-1,1′-binaphthyl **1**



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Scheme 3. Synthesis of the xerogel **2** by hydrolysis polycondensation of (*R*)-2,2′-(di-(3-triethoxysilyl)propyl-carbamoyloxy)-1,1′-binaphthyl **1**

The characterization of the hybrid solid by FT-IR and ^{13}C CP MAS NMR spectroscopy indicated that the chiral BINOL units are preserved in the gel after the hydrolysis–polycondensation procedure. The environment of silicon atoms can be detected by ^{29}Si CP MAS NMR spectroscopy.[27]

This method allows the distinction between silicon atoms attached to three [T-substructure, $RSiO_3$] or four oxygen atoms [Q-substructure, SiO_4] and gives qualitative information about their degree of condensation (T^m- and Q^n-resonances). ^{29}Si CP MAS spectra of the gels showed the resonance lines characteristic of the T^1-, T^2- and T^3-bridged silicon nuclei, corresponding to differently condensed substructures $R\mathbf{Si}(OSi)_x(OR)_{3-x}$ ($x=1$, 2, 3). The predominant environment of the silicon atoms in the gel corresponded to a T^3:$R\mathbf{Si}(OSi)_3$-coordination.

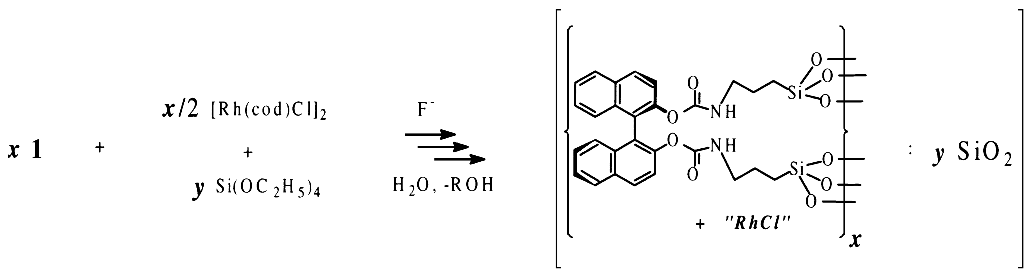
Nitrogen sorption experiments of the material[28] indicate the formation of a solid of low porosity with a BET surface lower than 10 m^2 g^{-1}.

These results demonstrate that the sol–gel procedure using nucleophilic catalysis of fluoride ions is a suitable method for the transformation of the silylated chiral BINOL precursor **1** into an organic–inorganic chiral hybrid network. The formed organic–inorganic hybrid materials, incorporating C_2-symmetric bis-carbamate binaphthyl units, have great potential in molecular recognition and may be suitable precursors for the elaboration of novel chiral phases as stationary phases for chiral HPLC or catalysis supports for enantioselective catalysis.

2.2. Immobilization of rhodium species in chiral gels

We focused here on the elaboration of new heterogeneous enantioselective catalyst systems, and investigated the incorporation of metal in the chiral hybrid matrix. We first studied the immobilization of rhodium species in the network.

Hybrid gels containing rhodium were obtained by hydrolyzing the (*R*)-BINOL precursor under conditions similar to those described above and in the presence of stoichiometric amounts of $[Rh(cod)Cl]_2$. We performed the condensation of the precursor in the presence of various amounts of added tetraethoxysilane (TEOS). This led to gels with different concentrations of the incorporated chiral organometallic moieties (Scheme 4). Gels formed within several hours. The gellification was accompanied by a strong colour deepening probably due to ligand exchange on rhodium. After curing for 5 days at room temperature, the deep red coloured gels were powdered and washed with THF in a soxhlet apparatus and finally were dried in vacuo at 110°C.



xerogel **3** : $x = 1, y = 0$

xerogel **4** : $x = 1, y = 2$

xerogel **5** : $x = 1, y = 4$

xerogel **6** : $x = 1, y = 10$

Scheme 4. Hydrolysis polycondensation of (*R*)-2,2′-(di-(3-triethoxysilyl)propyl-carbamoyloxy)-1,1′-binaphthyl **1** and tetraethoxysilane (TEOS) in the presence of $[Rh(cod)Cl]_2$

The characterization of the rhodium containing xerogels **3**–**6** by scanning electron microscopy (SEM) and elemental analysis confirmed the presence of rhodium(I) in the solids (Table 1). However, the Rh/Si ratios found in the hybrid materials were lower than those expected on the basis of the stoichiometry in the polycondensation mixture; 20–50% of Rh was lost during extraction probably by leaching. Only the rhodium species trapped in the hybrid network remained in the dried material. These results indicate that Rh is only weakly bound to the xerogel. The exact nature and structure of the embedded rhodium complex is not yet clear. It probably corresponds to a rhodium(I) species, since the rhodium/chlorine ratios found in the gels by scanning electron microscopy are close to one. Since the interaction of Rh with an (O–CO–NH)–carbamate group seems to be rather weak, we cannot exclude the interaction of the transition metal with other ligands than the carbamate functionality present in the network, e.g. the formation of Rh^I–O–Si-linkages, or the presence of physically embedded rhodium(I) species in the hybrid network.

Table 1
Xerogels prepared by hydrolysis polycondensation of (*R*)-2,2′-(di-(3-triethoxysilyl)propyl-carbamoyloxy)-1,1′-binaphthyl **1** and tetraethoxysilane (TEOS) in the presence of $[Rh(cod)Cl]_2$

xerogel	ratio ***x*** : ***y*** (polycondensation mixture)	Rh / Si ratio of the gels			Rh / Cl ratio of the gels
		calc.	SEM[a]	Elemental Analysis	SEM[a]
3	1 : 0	1 : 2	1 : 2.7	1 : 3.5	1.1
4	1 : 2	1 : 4	1 : 3.6	1 : 6	1.2
5	1 : 4	1 : 6	1 : 4.4	1 : 8.3	1.2
6	1 : 10	1 : 12	1 : 20.4	1 : 38	1.3

[a] Rh/Si- and Rh/Cl-ratios were determined by scanning electron microscopy

Further information on the nature of the incorporated rhodium species and on the structure of the hybrid network was available by solid state NMR analysis. ^{13}C CP MAS NMR spectra indicated that hybrid materials contained the chiral BINOL entity. The complete absence of signals in the domain between 80 and 100 ppm indicate that the cod ligand is lost and that Rh is no more complexed by cyclooctadiene. Characterization of the gels by ^{29}Si CP MAS spectroscopy showed the signals of the T^1-, T^2- and T^3-bridged silicon nuclei. As in the case of the gel **2** prepared without rhodium, the predominant environment of the silicon atoms in the xerogels **3**–**6** corresponds to a T^3:R**Si**$(OSi)_3$-coordination. The complete absence of Q-resonances (SiO_4 substructures) in the spectrum of xerogel **3** confirms that no Si–C cleavage occurred during the polycondensation procedure. The ^{29}Si CP MAS spectra of the xerogel **4** shows the additional Q-resonances of silicon attached to four oxygen atoms due to hydrolysis of TEOS (Fig. 1).

Nitrogen sorption experiments of the gels showed that by hydrolysis polycondensation of the pure BINOL-derived precursor lead to materials with low porosity similar to the xerogel **2** containing no rhodium. Mesoporous materials showing very broad pore size distributions (between 2 and 50 nm) were obtained by hydrolysis polycondensation of the precursor with various amounts of tetraethoxysilane (TEOS) (Table 2).

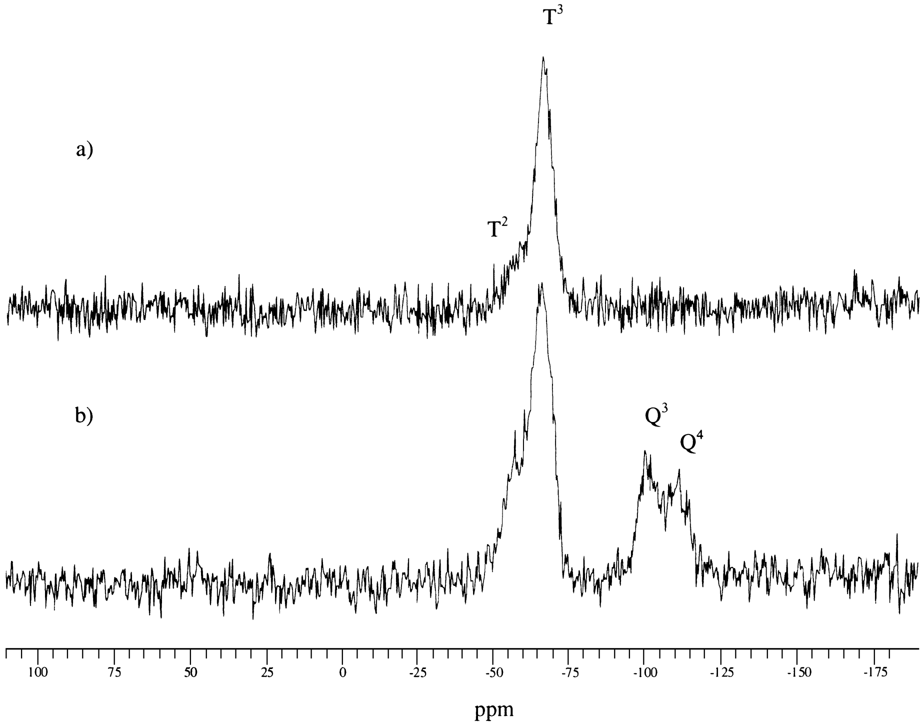


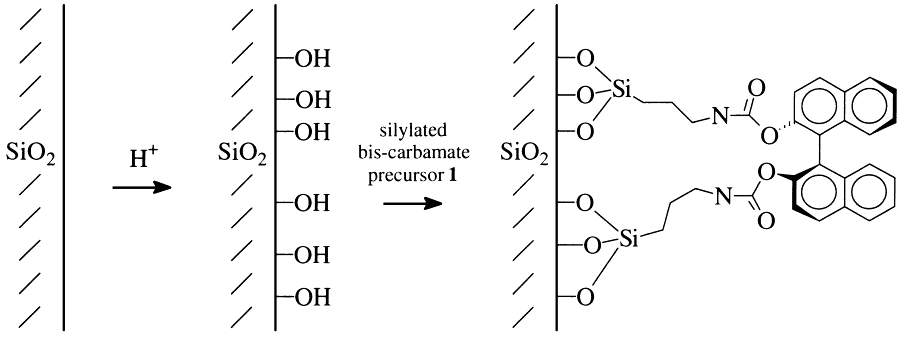
Figure 1. ^{29}Si CP MAS NMR spectra of xerogel **3** (a) and xerogel **4** (b)

Table 2
N_2 adsorption desorption data of the xerogels **3**–**6**

xerogel	BET surface area (m^2g^{-1})^a	Total pore volume (ml g^{-1})	pore diameter (nm)^b
3	0,9	-	-
4	10.5	-	-
5	170	0.46	polydisperse 5 - 30
6	88	0.14	polydisperse 2 - 50

[a] Determined by BET method.[29] [b]Determined by BJH method.[30]

We also prepared related materials for comparison of the catalytic properties. The silylated bis-carbamate precursor **1** was easily grafted onto a silica gel. We synthesized a silica gel-supported carbamate **7** by immobilization of the silylated precursor on the surface of a commercially available silica gel[31] following a classical procedure (Scheme 5). The grafted material shows a capacity of surface-immobilized carbamate of 0.41 meq/g. The solid was treated with a solution of $[Rh(cod)Cl]_2$ but no rhoduim was retained by the surface-immobilized carbamate. These results confirm that the interaction between rhodium and the immobilized chiral bis-carbamate is weak.



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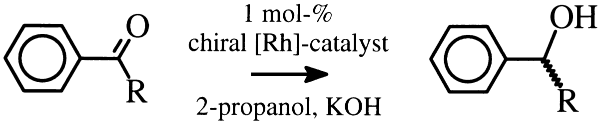
Scheme 5. Synthesis of a silica gel supported (*R*)-BINOL carbamate **7**

2.3. Catalytic properties of rhodium incorporating materials

The catalytic properties of the rhodium containing hybrid materials **3**–**6**, the molecular binol-bis-carbamate–rhodium complex **1-Rh** and the surface-immobilized carbamate–rhodium complex **7-Rh** were evaluated in hydrogen-transfer reduction of prochiral ketones[32,33] which was used here as a test reaction for the determination of activity (conversion) and selectivity (enantiomeric excess) of the catalysts (Scheme 6, Table 3).



Scheme 6. Hydride-transfer reduction of aromatic ketones

We examined the catalytic activity of the xerogels in the hydride-transfer reduction of acetophenone. All experiments were performed using 1 mol% of rhodium, the amount of solid catalyst was adjusted according to its rhodium content. Hybrid solids with high rhodium contents (i.e. xerogels **3**–**5**) showed high catalytic activity in hydride-transfer reduction of acetophenone (entries 1–3). The catalytic activity of the solid with low rhodium content (xerogel **6**, entry 4) was much lower.

We also studied the catalytic activity of related rhodium species. Firstly, the hydride-transfer reduction was performed using a 1:1 mixture of $[Rh(cod)Cl]_2$ and the molecular BINOL-trialkoxysilyl-carbamate **1** as catalyst in solution (entry 5). A low conversion (13%) was observed after 48 h at 60°C. Secondly, a rhodium containing solid was made by impregnation of the silica-supported carbamate **7** with $[Rh(cod)Cl]_2$. This impregnated material showed no catalytic activity in hydrogen-transfer reduction of acetophenone (Table 3, entry 6).

Regarding the selectivity, only the xerogel, in which the rhodium is trapped in an entirely chiral network (no added TEOS was used to prepare this material) lead to a significative enantioselectivity: 32% e.e. of (*R*)-1-phenylethanol was observed for the reduction of acetophenone

Table 3
Evaluation of the catalytic activity of the carbamates in hydride-transfer reduction of acetophenone (entries 1–6, 9–10), 1-acetonaphthone (entry 7) and *o*-methoxy-acetophenone (entry 8)

entry	**catalyst**	Evaluation		
		conversion (%)[a]	e. e. (%)[b]	configuration of the formed alcohol
1	xerogel **3**	94	32	*R*
2	xerogel **4**	95	3	*R*
3	xerogel **5**	95	8	*R*
4	xerogel **6**	12	0	
5	**1-Rh** (molecular carbamate-rhodium complex / homogeneous catalysis)	13	7	*R*
6	**7-Rh** (grafted carbamate – rhodium complex / impregnated solid)	7	0	
7	xerogel **3**	77	45	*R*
8	xerogel **3**	71	18	*R*
9	xerogel **3** / second cycle	36	~ 10	*R*
10	xerogel **8**	92	25	*S*

[a]Determined by GC using a HP-50+ column. [b]Determined by HPLC using a Daicel Chiralcel OD column. [c] 1-acetonaphthone was used; [d] *o*-methoxy-acetophenone was used.

(entry 1). This result was confirmed in the reduction of related ketones. The xerogel **3** also showed comparable activity and selectivity in the reduction of 1-acetonaphthone and *o*-methoxy-acetophenone (entries 7 and 8).

However, the embedded rhodium species appeared to be of low chemical stability. We tentatively recycled the xerogel **3** (entry 9), but in the second cycle the material showed much lower activity and selectivity. This may be due to a reduction of the rhodium species. The weak metal–ligand interaction in the material probably provides a very low stabilization of the rhodium(I) in the network.

Besides the xerogels **3**–**6**, which are based on (*R*)-BINOL-units, we also prepared a xerogel incorporating (*S*)-BINOL entities. Xerogel **8** was prepared similarly to xerogel **3** by hydrolysis–polycondensation of the only bis-silylated (*S*)-BINOL-precursor without added TEOS. It showed similar catalytic activity and selectivity as the latter and afforded (*S*)-1-phenylethanol in high yield and 25% e.e. (entry 10).

The obtained results show that a catalytic activity is only observed when the metal is embedded in the solid. Despite the materials exhibiting a low porosity (Table 2), the catalytic site located inside the hybrid network are accessible to the reactants. The behaviour of xerogel **6** appeared to be different from the xerogels **3**–**5**. The very low activity of this material may be related to the high dispersion of the BINOL-rhodium species for this hybrid solid prepared by using 10 mol of added TEOS. Although the nature of the rhodium complex is unclear, the BINOL-derived ligand is probably important in the stabilization of the catalytic species. Its low concentration in xerogel **6** led to poor stability of the catalyst. The low stability of the catalyst is also illustrated by the important loss of activity in the recycled material.

The main point concerns the selectivity of the catalytic material. Only the xerogels prepared upon hydrolysis condensation of the pure (*R*)- or (*S*)-BINOL ligands, led to enantioselective reduction although moderate e.e.s were obtained. This seems to be clearly related to the chiral structure of the hybrid network. The significative enantioselectivity, when xerogels **3** and **8** were used, can be attributed to a chiral matrix effect since: (i) the metal complex showed poor stability arising from a weak metal–ligand interaction; and (ii) low selectivity was observed with xerogels **4**–**6**. The dispersion of the chiral units in xerogels **4**–**6**, made with added TEOS, led to a completely different structure of the hybrid polymer and low or no enantioselectivity was observed. The local environment of the catalytic site is important in directing the selectivity of the reaction. The weak metal–ligand interaction probably contributes only to a small extent to the selectivity.

The chiral matrix effect observed with xerogels **3** and **8** is of interest for the preparation of catalytic materials. The design of enantioselective catalytic materials is a challenging area.[34] Chiral hybrid silica-based materials constitute a class of support which can be used for the immobilization of organometallic molecular species, and also for the dispersion of metal particles. We are currently investigating the use of silica hybrids as chiral supports for enantioselective heterogeneous catalysis. Additionally, hybrid systems containing chiral BINOL-derived carbamates are also promising solids for molecular recognition and chiral HPLC, as the carbamate functionality interacts with various substrates by hydrogen bonding. Carbamate-derived solids have been widely used as chiral stationary phases (CSPs).[35]

In conclusion, we have realized the facile synthesis of new (*R*)- and (*S*)-BINOL-derived chiral silylated precursors and their sol–gel transformation to give organic–inorganic hybrid materials. The materials incorporating rhodium show catalytic activity in hydride-transfer reduction of prochiral ketones. As interactions between the transition metal and the chiral ligand are weak, we attribute the observed enantioselectivity essentially to a supramolecular effect of the chiral tridimensional network. The hybrid catalysts have a low porosity which may limit the accessibility of the catalytic sites and the interaction between the substrate and the chiral hybrid solid. We are currently investigating control of the texture and morphology of the solids in order to improve the molecular recognition properties of this new class of chiral materials.

3. Experimental

All reactions were performed under a nitrogen or argon atmosphere using Schlenk tube techniques. ^{1}H, ^{13}C and ^{29}Si NMR spectra in solution were recorded on Bruker AC-200 and AC-250 spectrometers. [^{2}H]Chloroform was used as NMR solvent and chemical shifts are reported as δ values in parts per million relative to tetramethylsilane. *J* Values are in hertz. Solid-state ^{13}C and ^{29}Si NMR CP MAS spectra were recorded on a Bruker FT AM 200 apparatus. IR spectra were determined with a Perkin–Elmer 1000 FT-IR spectrometer. Melting points were determined with an Electrothermal IA9000 apparatus. Mass spectra were measured on a JEOL MS-DX 300 mass spectrometer. Optical rotations were measured on a Perkin–Elmer polarimeter 241. Elemental analysis were carried out by the 'Service Central de Micro-Analyse du CNRS'. BET measurements were performed with a Micromeritics Gemini 2360. For SEM analysis a LEICA S360 type Cambridge apparatus was used.

Enantiomeric excess were determined by HPLC analysis using a chiral cellulose carbamate-derived stationary phase (Chiralcel OD column) and hexane:2-propanol (9:1) mobile phase, UV detector 254 nm, flow 0.5 ml min^{-1}.

All solvents and reagents were obtained from commercial sources and used without purification, unless otherwise noted. In experiments requiring dry solvents, THF, toluene and diethyl ether were distilled over sodium/benzophenone, dichloromethane was distilled over P_2O_5 and alcohols were distilled over Mg turnings.

*3.1. (*R*)- 2,2′-(Di-(3-triethoxysilyl)propyl-carbamoyloxy)-1,1′-binaphthyl* ***1***

Under argon, 5.72 g (*R*)-2,2′-dihydroxybinaphthyl (20 mmol) were dissolved in a mixture of 50 ml of dichloromethane and 10 ml of triethylamine. To the homogeneous solution, 10.9 g (44 mmol) 3-(triethoxysilyl)propyl isocyanate were added by syringe at room temperature over a period of 10 min. The homogeneous solution was stirred over 4 h at room temperature. The coupling reaction can easily be monitored by infrared spectroscopy. After completion, solvents were pumped off and the crude product was dissolved in diethyl ether. The solvents were evaporated and the excess of 3-(triethoxysilyl)propyl isocyanate was distilled in vacuo. The crude product was dissolved in diethyl ether and filtered. Evaporation of the solvent gave the pure (R)-2,2′-(di-(3-triethoxysilyl)propyl-carbamoyloxy)-1,1′-binaphthyl as a colourless and highly viscous liquid. Yield: 15.2 g (19.4 mmol/97%). ^{1}H NMR (CDCl$_3$, δ) 0.45 (4H, m), 1.18 (18H, t, $J=7.0$ Hz), 1.39 (4H, m), 2.94 (4H, m), 3.75 (12H, q, $J=7.0$ Hz), 5.23 (2H, bt), 7.17–.30 (4H, m), 7.38–.46 (2H, m), 7.53 (2H, d, $J=8.8$ Hz), 7.90 (2H, d, $J=8.1$ Hz), 7.96 (2H, d, $J=8.8$ Hz); ^{13}C MR (CDCl$_3$, δ) 7.37, 18.26, 22.79, 43.31, 58.35, 122.38, 123.30, 125.26, 126.34, 126.46, 127.88, 129.22, 131.27, 133.34, 147.33, 154.65; ^{29}Si MR (CDCl$_3$, δ) –45.54 ppm; mass spectrum: *m*/*z* [FAB (+)] (%) 781 (7, M$^+$), 488 (98), 286 (100); $\nu_{\max}$ (KBr)/cm^{-1} 3333, 3059, 1748, 1532, 1509, 1222, 1166, 1103, 1078, 957, 772; $[\alpha]_D^{25}=-38.4$ (CH$_2$Cl$_2$, $c=0.993$).

(*S*)-2,2′-(Di-(3-triethoxysilyl)propyl-carbamoyloxy)-1,1′-binaphthyl **1** was prepared according to the same procedure as (*S*)-BINOL. The product shows identical properties to its enantiomer except the sign of specific rotation: $[\alpha]_D^{25}=+40.3$ (CH$_2$Cl$_2$, $c=0.957$).

*3.2. Hydrolysis–polycondensation of (*R*)-2,2′-(di-(3-triethoxysilyl)propyl-carbamoyloxy)-1,1′-binaphthyl: preparation of xerogel* ***3***

(*R*)-2,2′-(Di-(3-triethoxysilyl)propyl-carbamoyloxy)-1,1′-binaphthyl (917.3 mg/1.174 mmol) and chloro(1,5-cyclooctadiene)rhodium(I) dimer (290 mg/0.587 mmol) were dissolved in 4.3 ml of tetrahydrofuran at 40°C. After complete dissolution 45 µl of water and 23 µl of NH$_4$F 1 M were added. The homogeneous solution was allowed to stand at 40°C. A deeply red coloured gel was formed within 48 h. After ageing for 1 week, the solid was powdered, washed with ether, washed with tetrahydrofuran in a soxhlet extraction apparatus and finally dried in vacuum at 110°C. Yield: 0.505 g of a deep red coloured powder (62% yield based on $C_{28}H_{26}0_7Si_2$): FTIR (KBr) 3401 (ν_{Si-OH}), 2919/2870 (ν_{C-H}), 1719 ($\nu_{C=O}$), 1638 (ν_{N-H}), 1105 ($\nu_{Si-O-Si}$) cm^{-1}; ^{13}C CP MAS NMR δ 156.6, 148.2, 129.0, 43.7, 25.1, 9.7; ^{29}Si CP MAS NMR δ –65.6.

Xerogels **4**–**6** were prepared in a similar way. The exact quantities of the used reagents and yields are listened below:

Xerogel	precursor **1**	$[Rh(cod)Cl]_2$	TEOS	yield
3	0,5g/0,64mmol	158mg/0,32 mmol	0,28ml/1,28mmol	351mg / 67%
4	0,5g/0,64mmol	158mg/0,32 mmol	0,57ml/2,56mmol	448mg / 65%
5	0,5g/0,64mmol	158mg/0,32 mmol	1,43ml/6,4mmol	480mg / 58%

*3.3. Grafting of (*R*)-2,2′-(di-(3-triethoxysilyl)propyl-carbamoyloxy)-1,1′-binaphthyl on activated silica gel*

(a) Activation of silica gel: 4.00 g silica gel (Lichrosorb 60, Merck) were refluxed in hydrochloric acid (37%) for 4 h. The resulting white powder was washed with water and dried in vacuo for 24 h. Yield: 3.66 g.

(b) Grafting of (R)-2,2′-(di-(3-triethoxysilyl)propyl-carbamoyloxy)-1,1′-binaphthyl on activated silica gel: 2.00 g of activated silica gel was suspended in 15 ml of toluene. (*R*)-2,2′-(di-(3-triethoxysilyl)propyl-carbamoyloxy)-1,1′-binaphthyl (1.63 g, 2.1 mmol) was added and the resulting mixture was refluxed for 24 h. The solid was filtered and washed with toluene and acetone and dried overnight in vacuo. Yield: 2.45 g; ^{29}Si CP MAS NMR δ –46.5, –50.2, –57.7, –102.1, –110.6; anal. found: N, 1.17, corresponding to 0.41 meq/g.

3.4. Typical procedure for hydrogen-transfer reduction of acetophenone

3.4.1. Homogeneous reduction

A solution of $[Rh(cod)Cl]_2$ (43 mg, 0.086 mmol) and 135 mg (*R*)-2,2′-(di-(3-triethoxysilyl)-propyl-carbamoyloxy)-1,1′-binaphthyl (0.17 mmol) in 2-propanol was degassed and stirred for 30 min. Then KOH (48 mg, 0.86 mmol) were added and the reaction mixture was stirred for an additional 30 min. Acetophenone (2.0 ml/17 mmol) was then added and the mixture was stirred for 48 h at 60°C under nitrogen. The reaction was monitored by capillary gas chromatography and the enantiomeric excess were measured by HPLC using a Daicel Chiracel OD column.

3.4.2. Heterogeneous reduction

Hybrid Cogel complex (8.3×10^{-5} mol of rhodium that is 1 mol%) was dried under vacuum for 3 h. Then degassed 2-propanol (20 ml) and KOH (20 mg, 0.35 mmol) was added under an inert atmosphere. The reaction mixture was stirred for 1 h and then the ketone (8.3 mmol) was introduced with a syringe. The reaction mixture was stirred for 48 h at 60°C under nitrogen. The reaction was monitored by capillary gas chromatography and the enantiomeric excess was measured by HPLC using a Daicel Chiracel OD column. The results are shown in Table 3.

References

1. Brinker, C. J.; Scherer, G. W. *Sol–Gel Science: the Physics and Chemistry of Sol–gel processing*; Academic Press: San Diego, 1990, and references cited therein.
2. Schmidt, H. *Mater. Res. Soc. Symp. Proc.* **1990**, *180*, 961, and references cited therein.

3. Sanchez, C.; Ribot, F. *New J. Chem.* **1994**, *18*, 1007, and references cited therein.
4. Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. *Chem. Rev.* **1995**, *95*, 1409.
5. (a) Shea, K. J.; Loy, D. A.; Webster, O. W. *Chem. Mater.* **1989**, *1*, 572; (b) Shea, K. J.; Loy, D. A.; Webster, O. W. *J. Am. Chem. Soc.* **1992**, *114*, 6700; (c) Loy, D. A.; Shea, K. J. *Chem. Rev.*, **1995**, *95*, 1431, and references cited therein.
6. (a) Corriu, R. J. P.; Moreau, J. J. E.; Thépot, P.; Wong Chi Man, M. *Chem. Mater.* **1992**, *4*, 1217; (b) Corriu, R. J. P.; Leclercq, D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1420, and references cited therein.
7. (a) Corriu, R. J. P.; Hesemann, P.; Lanneau, G. F. *Chem. Commun.* **1996**, 1845; (b) Corriu, R. J. P.; Moreau, J. J. E.; Thépot, P.; Wong Chi Man, M.; Chorro, C.; Lère-Porte, J.-P.; Sauvajol, J. L. *Chem. Mater.* **1994**, *6*, 15.
8. Loy, D. A.; Jamison, G. M.; Baugher, B. M.; Myers, S. A.; Assink, R. A.; Shea, K. J. *Chem. Mater.* **1996**, *8*, 656.
9. (a) Roger, C.; Hampden-Smith, M. J.; Brinker, C. *J. Mater. Res. Symp. Proc.* **1992**, *271*, 51; (b) Lu, Y.; Cao, G. Z.; Kale, R. P.; Delattre, L. L.; Brinker, C. J.; Lopez, G. P. *J. Mater. Res. Symp. Proc.* **1996**, *435*, 271.
10. Loy, D. A.; Buss, R. J.; Assink, R. A.; Shea, K. J.; Oviatt, H. *Polym. Prep.* **1993**, *34*, 244.
11. (a) Corriu, R. J. P.; Moreau, J. J. E.; Thépot, P.; Wong Chi Man, M. *Chem. Mater.* **1996**, *8*, 100; (b) Chevalier, P.; Corriu, R. J. P.; Delors, P.; Moreau, J. J. E.; Wong Chi Man, M. *New J. Chem.* **1998**, *22*, 423.
12. Barton, T. J.; Bull, L. M.; Klemperer, W. G.; Loy, D. A.; McEnaney, B.; Misono, M.; Monson, P. A.; Pez, G.; Scherer, G. W.; Vartuli, J. C.; Yaghi, O. M. *Chem. Mater.* **1999**, *11*, 2653.
13. Schubert, U. *New J. Chem.* **1994**, *18*, 1049, and references cited therein.
14. Moreau, J. J. E.; Wong Chi Man, M. *Coord. Chem. Rev.* **1998**, *178–180*, 1073.
15. Adima, A.; Moreau, J. J. E.; Wong Chi Man, M. *J. Mater.Chem.* **1997**, *7*, 2331.
16. Lin Pu *Chem. Rev.* **1998**, *98*, 2405.
17. Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581.
18. Kobayashi, M.; Araki, M.; Hachiya, I. *J. Org. Chem.* **1994**, *59*, 3758.
19. Ishihara, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1994**, *116*, 1561.
20. Sasai, H.; Arai, T.; Satow, Y.; Houk, K. N.; Shibasaki, M. *J. Am. Chem. Soc.* **1995**, *117*, 6194.
21. Kobayashi, S.; Suda, S.; Yamada, M.; Mukaiyama, T. *Chem. Lett.* **1994**, *97*, 1.
22. Mikami, K. *Pure Appl. Chem.* **1996**, *68*, 639.
23. Corey, E. J.; Barnes-Seeman, D.; Lee, T. W.; Goodman, S. N. *Tetrahedron Lett.* **1997**, *38*, 6513, and references cited therein.
24. Bougauchi, M.; Watanabe, S.; Arai, T.; Sasai, H.; Shibasaki, M. *J. Am. Chem. Soc.* **1997**, *119*, 2329.
25. Sasai, H.; Tokunaga, T.; Watanabe, S.; Suzuki, T.; Itoh, N.; Shibasaki, M. *J. Org. Chem.* **1995**, *60*, 7388.
26. Corriu, R. J. P.; Leclercq, D.; Vioux, A.; Pauthe, M.; Phalippou, J. *Ultrastructure Processing of Advanced Materials*; Mackenzie, J. D.; Ulrich, D. R., Eds.; John Wiley & Sons: New York, 1988; p. 113.
27. Maciel, G. E.; Sindorf, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 7606.
28. Greqq, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*; Academic Press: London, 1982.
29. Brunauer, S.; Emmett, P. H.; Teller, J. E. *J. Am. Chem. Soc.* **1938**, *60*, 309.
30. Barrett, E. P.; Joyner, C. G.; Hallenda, P. P. *J. Am Chem. Soc.* **1951**, *73*, 373.
31. Soai, K.; Watanabe, K.; Yamamoto, A. *J. Org. Chem.* **1990**, *55*, 4832.
32. Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, ***30***, 97, and references cited therein.
33. Gamez, P.; Fache, F.; Lemaire, M. *Tetrahedron: Asymmetry* **1995**, *6*, 705.
34. Blaser, H. U. *Tetrahedron: Asymmetry* **1991**, *2*, 843.
35. Castells, C. B.; Carr, P. W. *Anal. Chem.* **1999**, *71*, 3013.