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Molecular imprinting of polymerised catalytic complexes in asymmetric catalysis

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Abstract

The hydride transfer reduction of prochiral ketones using rhodium based catalysts has been studied. In homogenous catalysis, acetophenone was quantitatively converted to (*R*) phenyl ethanol 3 in 7 days, (67% ee) using two equivalent of (1*S*,2*S*)-*N*,*N*′-dimethyl-1,2-diphenylethane diamine per Rh. We then prepared polyurea supported complex: rhodium containing catalyst were prepared by complexation of the metal to nitrogen ligands in the backbone. Using this catalyst, acetophenone was quantitatively converted to (*S*) phenyl ethanol in 1 day, enantiomeric excess was 60%. We have then polymerised preformed [rhodium(I)-(*N*,*N*′-dimethyl-1,2-diphenylethane diamine)$_2$] with di- and triisocyanates. Using the (*S*,*S*) isomer of the diamine leads to the reduction of propiophenone into (*R*) in 6 days with 47% ee In order to use molecular imprinting effect, we have polymerised [rhodium(I)-(*N*,*N*′-dimethyl-1,2-diphenylethane diamine)$_2$] in the presence of a chiral template: pure (*R*) or (*S*) sodium phenylethanolate. Reduction of various substrates was carried out. We have shown that the imprinting effect is obvious for molecule related in structure to the template (propiophenone, 4′-trifluoromethyl acetophenone) and it is not efficient if the substrate has a structure too different from the template one. The studying of conversion vs. global conversion has shown that the mechanism occurs via two parallel reactions on the same site without any interconversion of the final products. Phenyl ethyl ketone was reduced quantitatively in 2 days to (*R*) phenyl ethanol ee 70%.

Keywords: Asymmetric catalysis; Molecular imprinting; Rhodium; Ketone reduction

1. Introduction

With the recent progresses in molecular imprinting, one can consider this as a new tool to synthesise enantioselective material applicable to both chromatography separation and catalyst preparation [1].

The most studied and most successful application of molecular imprinted polymers (MIP) is their use as material for chromatography. Especially, resolution of racemate in HPLC has proven to be a useful application [2].

Since MIPs have functional groups arranged in such a manner that they are complementary in shape and electronic features to the template, a logic step is to perform reaction within the MIPs, since the substrate is forced into a specific conformation. Wulf and Vietmeier have prepared L-threonine with an enantiomeric ex-

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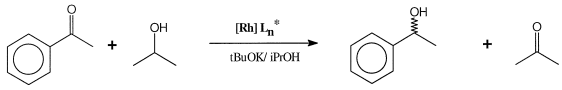


Scheme 1. Hydride transfer reduction of phenyl alkyl ketone.

cess of 36% by using a polymer which was imprinted with L-DOPA [3]. The cavities of the polymer contained a salicylaldehyde and a phenylboronic acid moiety each. L-Threonine is prepared by reaction of the polymer bound anion of a salicylideneglycine nickel complex with acetaldehyde.

The target reaction in this study is the reduction of prochiral ketones. In order to do so, we chose to use hydride transfer reduction to reduce phenyl alkyl ketones. This technique is attractive because one can avoid high pressure and the use of H_2. Reduction is carried out using a hydride donor solvent (mainly isopropanol). Under basic conditions, in the presence of a rhodium catalyst, ketones are reduced in alcohol and isopropanol is oxidised in acetone (Scheme 1).

The use of chiral ligands within the rhodium complex can render the catalyst enantioselective. For example, Gladiali et al. and Zassinovich et al. have reduced acetophenone to (*S*)-1-phenylethanol (ee 63%, yield 89%) using a catalyst having chiral alkyl phenantroline ligands [4,5]. More recently, Ohkuma et al. and Hashiguchi et al. have reported that various substituted 1-phenylethanols are obtained in high yields and with up to 97% ee using ruthenium complexes having a tetradentate ligand: *N*-(toluene-*p*-sulfonyl)-1,2-diphenylethylenediimine or *N*-(toluene-*p*-sulfonyl)-1,2-diphenylethylenediamine [6,7].

2. Experimental

The polymerised complex was prepared as described below for the molecular imprinted one but without chiral template.

A typical procedure for imprinted polymerised rhodium complex synthesis is: in a round bottom flask under inert dry atmosphere of argon, 750 mg (3.12 mmol) of (1*S*,2*S*)-*N*,*N*′-dimethyl-1,2-diphenylethane diamine was dissolved in 4 ml of dichloromethane freshly distilled on P_2O_5. Seventy-eight milligrams (0.32 mmol) of catalytic precursor ($[Rh(C_8H_{12})Cl]_2$) are added and the solution stirred.

Preparation of sodium 1-phenylethanolate: 9 mg (0.33 mmol) of NaH 98% are introduced in a second round bottom flask. Then, 1.5 ml of dichloromethane freshly distilled on P_2O_5 and 36 μl (0.3 mmol) of optically pure (*R*)-1-phenylethanol are added. This solution is stirred for 1 h before being introduced into the flask containing the rhodium complex. After 2 h stirring, a solution of diisocyanate (**4a** or **4b**) and triisocyanate ($[-C_6H_3(NCO)CH_2-]n$, $n = 3$ (Aldrich 11,130-9)) in 1.5 ml of dichloromethane is added. The polyaddition is exothermic. The solution is stirred overnight at room temperature. The solvent is evaporated and the polymer is crushed and washed with 500 ml of 2-propanol during 24 h. Finally, it is filtered through a Millipore filter (vv type, pore size 0.10 μm). Elimination of the imprinted alcohol is monitored by GC on a chiral Cydex B SGE column, 25 m $\times$ 0.25 mm using the other enantiomer as internal reference. The material is then dried and sifted. Only particles with a size between 80 and 120 μm were retained. Elemental analy-

Table 1
Influence of the nature of stirring

Stirring	Conversion[a]	ee (*R*)	Initial speed (mmol h^{-1} g^{-1} of Rh)	Regime
Magnetic	11	46	0.21	diffusion
Vibrator	4	45	0.20	diffusion
Reactivial®	33	51.5	0.91	chemical

[a]After 10 h reaction.

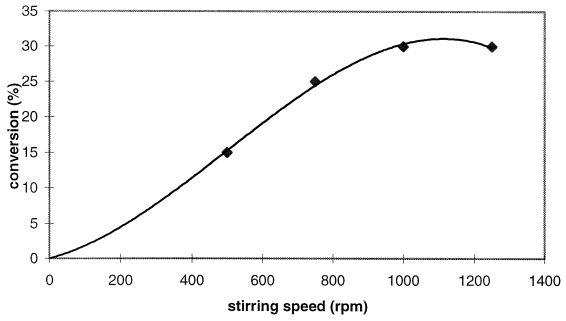


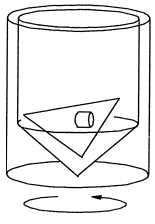
Fig. 1. Conversion vs. stirring speed for Reactivial after 10 h reaction.

sis of the solvent shows no evidence for the presence of rhodium, therefore, it can be assumed that no leaching of the metal occurs.

2.1. Influence of the nature of the stirring

Influence of the nature of the stirring is reported in Table 1. First experiments were carried out in a 25 ml one neck round bottom flask with magnetic stirring. Studding influence of the stirring speed showed that could not get rid off diffusion (initial speed is increasing with the stirring speed). In addition, at high stirring speed (1000 rpm) polymer is crushed and reaction stops after 3 h.

We have then ensured agitation using a vibrator, but once again, we could not obtain the diffusion regime. At the end, the utilisation of a Reactivial® allows us to obtain a good initial speed and to eliminate the diffusion problems without destroying our catalyst (same conversion at 1000 and 1250 rpm (Fig. 1)). Further reaction were carried out using Reactivial® (Scheme 2).



Scheme 2. Schematic view of a Reactivial®.

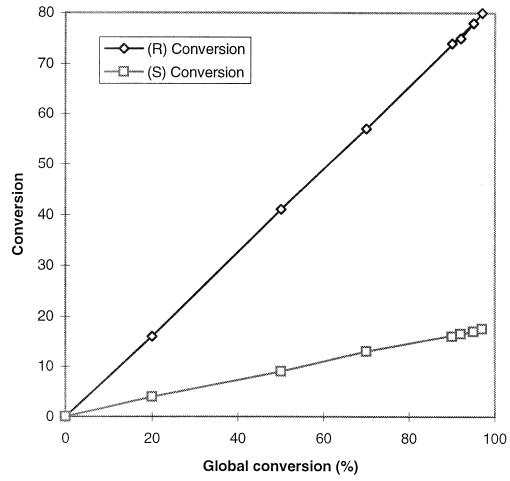


Fig. 2. Example of conversion vs. global conversion graph.

2.2. Conversion and reproducibility

One can note that troubles with reproducibility were observed during utilisation of MIP. A determined catalyst would always have the same selectivity, but activity would dramatically change with the age of catalysts (the older the catalyst the lower the activity). One can assume that Rh(I) evolves during time to form an inactive species. This can explain the loss of activity without variation in selectivity.

In order to determine when enantiomeric excess variations were due to the nature of the catalyst and when it was just due to the measurement we have evaluate GC margin of error.

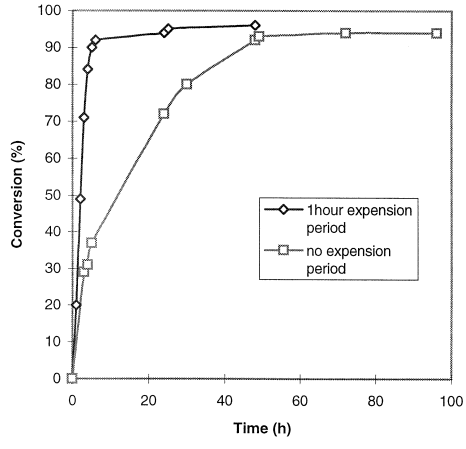
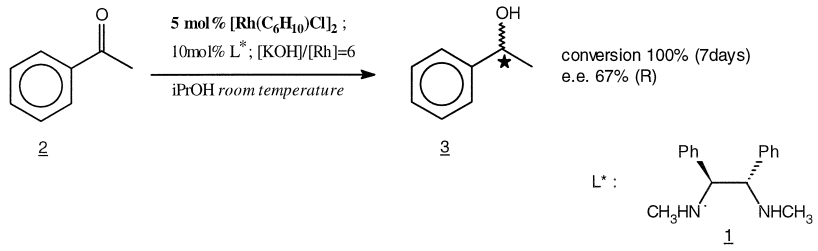


Fig. 3. Influence of expansion period on activity.



Scheme 3. Homogeneous phase-reduction of acetophenone.

Ten successive measurements were done on GC on a chiral Cydex B SGE capillary column, 25 m $\times$ 0.25 mm Φ with a racemate of phenyl propanol. We have then determined that error is $\pm$0.75%. Therefore, all further enantiomeric excesses will be given $\pm$1%.

2.3. Calculation of the enantiomeric excess

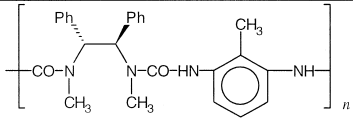
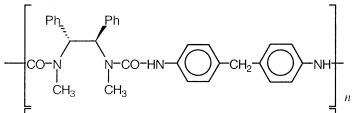
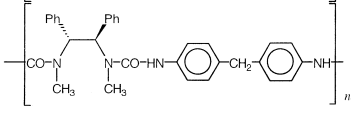
Plotting conversion vs. global conversion graphs, we always obtain linear graphs (whatever the value of the parameters) with a very high correlation as it is shown on Fig. 3. No by-product was detected by GC-MS and thin layer chromatography. Therefore, one can note that the difference of the slopes of the (R) and (S) enantiomers gives an estimation of the enantiomeric excess. The sum of the two enantiomers will always be 100%. The interesting point is to have a linear relation as detailed later. This gives a useful tool to determine statistically the selectivity of our system. We will use this measure for the next part of this study.

3. Results

3.1. Homogeneous reduction [8]

Despite the fact that our main goal is to perform heterogeneous catalysis, our first step was to reduce acetophenone 2 selectively with homogeneous catalysis in order to better know our system. We have chosen to use diamine ligands owning one C_2 axis. When nitrogen

Table 2
Reduction of acetophenone using polyurea-based supported rhodium complexes

Entry	Chiral Polymer -Rh Catalyst*	Conv. (%)	Time (days)	Cross-linking	e.e. (%) (Configuration)
1		63	17	no	24 (R)
2		97	3	no	39 (R)
3		100	1	yes	60 (R)

* All results at 70°C.

atoms have two identical substitutes (H or CH_3), resulting complexes are poorly selective. Best results were obtained using two equivalents of diamine 1 per rhodium. Acetophenone 2 was quantitatively converted to (*R*) phenyl ethanol 3 in 7 days, enantiomeric excess was 67% [8] (Scheme 3).

3.2. Polyurea-supported complex [9]

Because amines functions can react with isocyanates to give urea, we have prepared polyurea using chiral diamines previously described and diisocyanates. We have already described properties of theses polyureas with pseudo C_2-axis of symmetry [10].

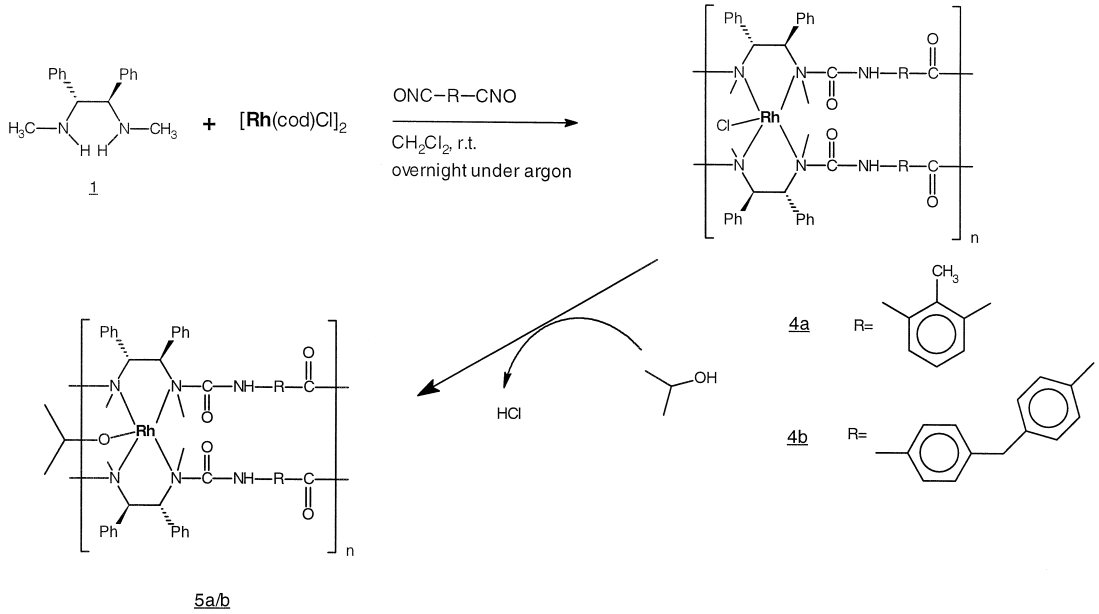
Rhodium-containing catalyst was prepared by complexation of the metal to nitrogen ligands in the backbone ([diamine unit]/[Rh] = 10). To this end, $[Rh(COD)Cl]_2$ was added to the slurry of the polymer in propan-2-ol. After 24 h stirring at room temperature, the catalyst was filtered off, washed thoroughly with propan-2-ol and dried under vacuum. Elemental analysis confirms that rhodium is complexed quantitatively (due to poor precision of metal analysis in a polymer, difference between calculated and found amount is not significant).

ANAL: calc. Rh% = 2.41; found Rh% = 2.01

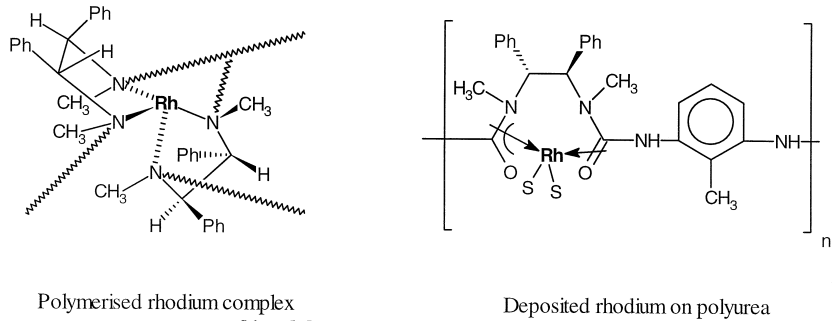
These polyurea-based catalysts were involved in acetophenone reduction (Table 2) at 70°C because speed rate was dramatically low at room temperature.

The first point to mention is the fact that using homogeneous and heterogeneous catalysis leads to inverted selectivity as (*S*) enantiomer is mainly obtained using homogeneous catalyst rather than (*R*) enantiomer is preferentially formed using heterogeneous one. This brings to evidence that active sites are very different in these two systems.

Entry 3 which shows the best results (60% of enantiomeric excess) was carried out using a polymer cross-linked. It was prepared using crude methylenediisocyanate which is a commercial mixture of pure MDI (60%) and triisocyanates (30%) (Merck Art. 820797). This result has to be compared with the one from entry 2 (39%) which uses the same diamine and diisocyanates but without cross-linkers. Therefore, it seems that the rigidity of the active site



Scheme 4. Polymerisation of a preformed diamine–rhodium complex.



Scheme 5. Proposed structures for heterogeneous complexes.

is crucial for the selectivity of the catalytic system.

3.3. Polymerisation of a preformed diamines–rhodium complex

In order to use 'molecular imprinting effect', we have to prepare a complex that we can polymerise in situ. That means that rhodium has to be enclosed inside the polymer during the synthesis and not deposited on it as previously described [9].

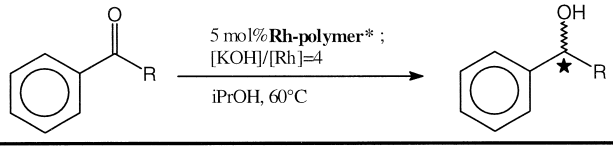
We have developed here a new method for preparation of heterogeneous catalyst. It consists of immobilising a preformed [rhodium(I)-(*N,N′*-dimethyl-1,2-diphenylethane diamine)$_2$] complex by polyaddition with a mixture of di- and triisocyanates (Scheme 4).

Then, this new material could be used as catalyst in hydride transfer reduction.

One can note that whereas with deposited rhodium on chiral polymer opposite enantio-differentiation was obtained, with polymerised complexes, same enantiomer with the one obtained by homogeneous catalysis is preferentially produced (entries 1 and 2). This can be explained by a distinct complexation of rhodium. When catalysts were obtained by deposition of rhodium(I) on polyurea synthesised beforehand, the low mobility of the polymer chain allows the coordination of only two nitrogen atoms to the metal (see Scheme 5). Catalysts obtained with the new method should have a structure close to the one working in homogenous phase because polymerisation is carried out around this complex (Table 3).

Polymerised (*R,R*) rhodium complex (entry 1) allows a lower selectivity of the same enantiomer to that observed in homogeneous phase. The same phenomena is observed with the

Table 3
Reduction of ketones with polymerised complexes



Entry	Polymer	R	Catalyst	Inductor config.	Conversion (%)	Time (days)	e.e. (%) (Config.)
1	5a	"	heterogeneous	(*R,R*)	44	1	33 (*S*)
2	5b	"	heterogeneous	(*S,S*)	98	1	25 (*R*)
3	5b	C_2H_5	"	(*S,S*)	96	6	47 (*R*)[a]

[a] reduction realised at 25°C.

[a]Reduction realised at 25°C.

(1*S*,2*S*)-*N*,*N*′-dimethyl-1,2-diphenylethane diamine (entry 2).

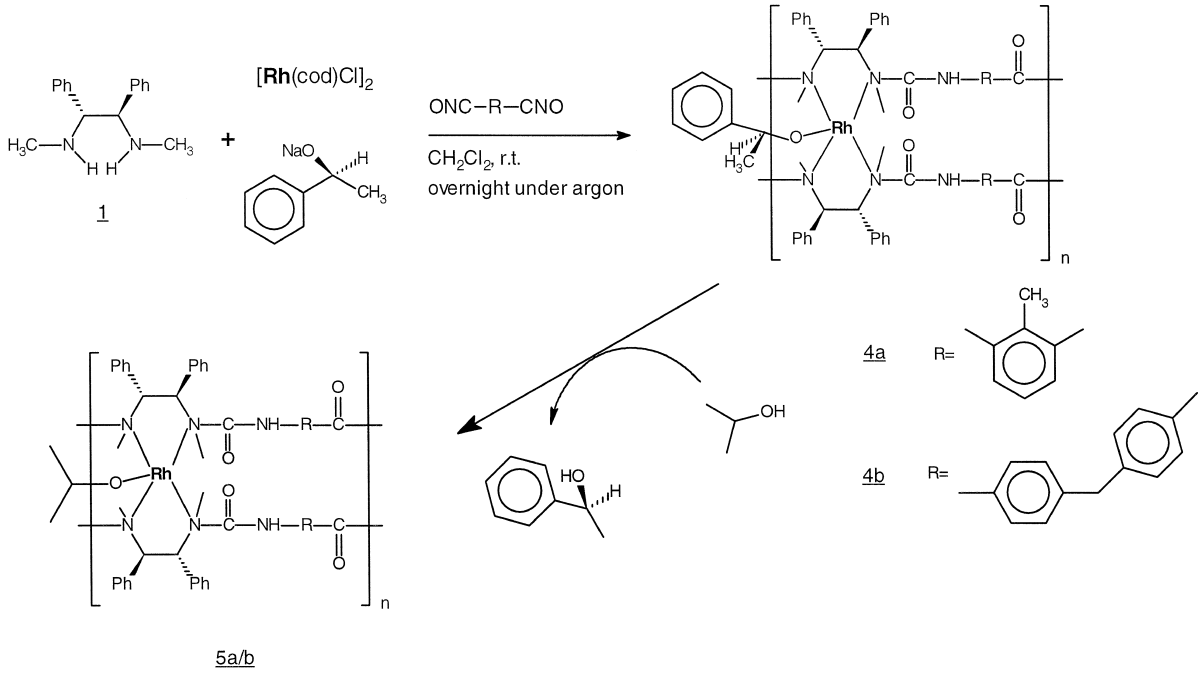
In order to determine versatility of our material, we have reduced with the same polymer **5b**, propiophenone which is sterically close to acetophenone. Reaction seems to be more selective but slower. Increase of selectivity can be explained by a stronger differentiation between (*R*) and (*S*) 1-phenylpropanol than between (*R*) and (*S*) 1-phenylethanol.

3.4. Molecular imprinting effect

We wish to use 'molecular imprinting effect' to reach highly enantioselective catalytic reaction. The new catalyst preparation described previously allows us to polymerise the chiral rhodium complex in the presence of optically pure 1-(*S*)-phenylethanol as template in order to increase enantioselectivity. Scheme 6 describes the principle: [bis(diamine 1) rhodium] complex is prepared in a dichloromethane solution of sodium 1-(*S*)-phenylethanolate. It is then polymerised by addition of di- and triisocyanates. The imprinted polymer is then washed with excess of 2-propanol in order to eliminate the template (elimination is monitored by GC on a chiral Cydex B SGE column, 25 m × 0.25 mm *Φ* with the other enantiomer as internal reference). The polymer is then dried and used in transfer reduction.

The polymerised [bis-((*R*,*R*)-diamine 8)-1-(*S*)-phenylethoxy-rhodium] complex allows an increase of 10% ee in imprinted alcohol whereas the utilisation of [bis-((*R*,*R*)-diamine 8)-1-(*R*)-phenylethoxy-rhodium] complex shows a light decrease of it (entries 2 and 3). These results may represent an imprinting effect. The rigid cross-linked polymer **5b** permits an increase of 18% ee in the case of reduction of acetophenone (entries 4 and 5) (see Table 4).

To be sure that the increase of enantioselectivity observed is not due to a leaching of left template, we have performed reduction onto propiophenone as we already knew non-imprinted complexes are selective for this compound (Table 3). A similar increase of 19% ee between non-imprinted and imprinted polymer



Scheme 6. Molecular imprinted polymer preparation.

Table 4
Molecular imprinting effect in reduction by using Rh catalyst

Entry	Polymer	R	Catalyst	Inductor configuration	Conversion (%)	Time (day)	ee (%) (Configuration)
1	**5a**	CH_3	polymerised	(*R*,*R*)	44	1	33 (*S*)
2	**5a**	CH_3	(*S*) templated	(*R*,*R*)	42	1	43 (*S*)
3	**5a**	CH_3	(*R*) templated	(*R*,*R*)	40	1	30 (*S*)
4	**5b**	CH_3	polymerised	(*S*,*S*)	98	1	25 (*R*)
5	**5b**	CH_3	(*R*) templated	(*S*,*S*)	98	1	43 (*R*)
6	**5b**[a]	C_2H_5	polymerised	(*S*,*S*)	96	6	47 (*R*)[b]
7	**5b**[a]	C_2H_5	(*R*) templated	(*S*,*S*)	91	9	66 (*R*)[b]

[a] Cross-linking ratio is 47/53.
[b] Reduction realised at 25°C.

is observed (entries 6 and 7). This cannot be due to any leaching as (±)-1-phenyl-propanol is not present into initial catalyst (Table 4). Therefore, further trials were then carried out using (*R*)-1-phenylethanol as template and propiophenone as substrate to insure that observed enantioselectivity is only due to the selectivity of the system.

3.5. Influence of temperature and swelling of the polymer

Increasing the temperature increases the selectivity of the reaction: Carrying reduction using a 40/60 cross-linked polymer and moving from room temperature to 60°C leads to an increase of the enantiomeric excess from 46 to 61%. This can be explained by the fact that the hot solvent (isopropanol) makes the polymer expand and then 'core' sites can be reached by the substrate.

There, cavities have a better defined shape making the system more selective. Therefore reaction should be performed at 60°C rather than at room temperature. The swelling–selectivity relationship is not absolute, the use of a very polar solvent such as *N*,*N*-dimethylacetamide, leads to such a swelling of the polymer that no more selectivity is observed. Thus, one can assume that this increase of selectivity is due to an equilibrium between accessibility of the best defined sites of the system and stiffness of these sites. The activity–swelling relationship is corroborated by the fact that the polymer is more active if it is left for 1 h in hot solvent before starting the reaction rather than if the reaction is started as soon as catalyst is in the reactor (Fig. 6). The pre-expansion period is once again to the benefit of activity (see Fig. 2).

One can notice that with the homogeneous catalyst, enantiomeric excess drop from 67% at room temperature to 55% at 60°C [9]. This is even more in favour of the swelling of the polymer responsible of the increase of selectivity as consequence of a better accessibility of the best active sites.

Table 5
Cross-linking-ratio influence

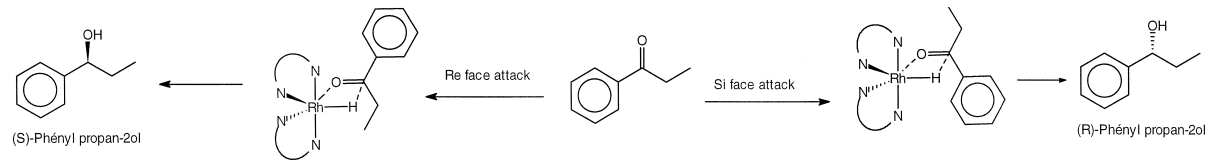
Entry	Cross-linking ratio	$ee_{(R)}$
1	30/70	55
2	40/60	60
3	*50/50*	*70*
4	80/20	65

3.6. Influence of cross-linking ratio

The amount of cross-linker defines the stiffness of the MIP. Therefore one should involve enough cross-linkers to have a polymer with a sufficient rigidity to obtain selectivity but not too much to keep a good accessibility to the reaction sites.

It seems that the best results were obtained with a cross-linking ratio [2] of 50/50. Then, the

[2] Ratio calculated as: cross-linking ratio = [sum of functional groups from triisocyanates]/[sum of functional groups from diisocyanates].



Scheme 7. Proposed mechanism of reaction.

selectivity is 70% of enantiomeric excess (see Table 5).

3.7. Mechanism

We always obtain linear graphs (whatever the value of the parameters) for conversion vs. global conversion graphs.

On Fig. 3, a slope of 82% ($r = 1$) for the *R* enantiomer and a slope of 18% ($r = 0.998$) for the *S* enantiomer are observed. Consequently, one can assume that the synthesis of the two enantiomers occurs via two parallel reactions on the same site without any interconversion.

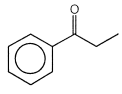
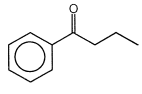
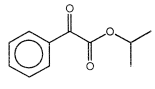
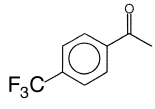
We have therefore proposed the following mechanism (Scheme 3): propiophenone approaches the hydride rhodium complex (described by Gladiali et al. and Zassinovich et al. [4,5]) facing its Si or Re side. This leads to two different complexes and gives (*R*) or (*S*) phenyl propan-1-ol. The shape and electronic features of the cavity where the rhodium complex is, should influence the activation energy of these intermediates, thus promoting one of them to react much faster than the other(the one that is created by the Si side approach). (*R*)-1-phenyl-propanol synthesis is favoured (Scheme 7).

3.8. Selectivity and activity of MIP on different substrates

We have then reduced substrates with structure more or less close to the acetophenone one (Table 6). Conditions were: 60°C temperature, 1 h pre-expansion, cross-linking ratio 50/50, [*t*BuOK]/[Rh] = 6.

It can be seen that for 4′-trifluoromethyl acetophenone (entry 4), the initial rate is higher than for the other compounds. It seems that there is an activation of the ketone group by the

Table 6
Hydride transfer reduction of different substrates

		imprinted Polymer		non imprinted Polymer	
Entry	**Substrates**	initial speed mmol.h^{-1}.g^{-1} of Rh	e.e.$_{(R)}$	initial speed mmol.h^{-1}.g^{-1} of Rh	e.e.$_{(R)}$
1		18.3	70	1.5	48
2		14.7	44	5.2	58
3		-	-	-	-
4		64	38	10	30

three fluorine atoms through the aromatic ring. At the other end, no conversion was observed for isopropyl-formiate-benzoyle (entry 3). This can be attributed to the low activity of the α-keto-ester-group or because of the insolubility of the molecule in the polymer.

Moving from propiophenone to butyrophenone (entry 2), activity goes down from 18.3 to 14.7 mmol h^{-1} g^{-1} of Rh. We can say that the longer the lateral chain the lower the reactivity.

For entries (1) and (4), we have obtained an imprinted effect. The selectivity is different and depends of the structure of the substrate. An increase of 22 points was observed for propiophenone and of 8 points for 4′-trifluoromethyl acetophenone. The lower imprinting effect for 4′-trifluoromethyl acetophenone could be explained by the structure being less similar to that of acetophenone than with the propiophenone, and because of the high activity of the molecule.

Not only are molecular imprinted polymers more selective, but they are also more active (5 to 10 times higher).

For propyl-phenyl ketone (entry 2), a decrease of 14% ee on the selectivity was observed. This can be explained by the structure of this compound which is too far from the acetophenone one. A mismatch effect is observed.

4. Conclusion

We have prepared an efficient homogeneous catalyst for hydride transfer reduction by using rhodium metal and two N,N'-dimethyl-1,2-diphenylethane diamine molecule as chiral ligand. We have then shown that it is possible to obtain efficient heterogeneous catalysts by depositing rhodium on chiral polyureas with pseudo-C_2-axis. Polymerised preformed [(N,N'-dimethyl-1,2-diphenylethane diamine)$_2$Rh] complex allows us to obtain enantioselective materials. We have then shown that it is possible to imprint an optically pure template in the rhodium-organic matrix and to use the heterogeneous catalyst in asymmetric catalysis with an obvious template effect. We have then brought to evidence that the stirring has a strong influence on the system. The studying of conversion vs. global conversion has shown that the mechanism occurs via two parallel reactions on the same site without any interconversion of the final products. Adjusting the cross-linker ratio at 50/50 allows us to find a compromise between activity and selectivity. Phenyl ethyl ketone (propiophenone) was reduced quantitatively in 2 days to (R)-1-phenyl propanol with 70% enantiomeric excess. We have then shown that the imprinting effect is obvious for molecule related in structure to the template (propiophenone, 4′-trifluoromethyl acetophenone) and it is not efficient if the substrate has a structure too different from the template one.

Further experiments on using these type of materials and on polymers prepared without chiral monomers are under investigation.

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