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Clay-supported bis(oxazoline)–copper complexes as heterogeneous catalysts of enantioselective cyclopropanation reactions

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Abstract

Several chiral bis(oxazoline)–copper complexes are supported by cation exchange in laponite, bentonite and K10 montmorillonite, and their catalytic performances are compared in the benchmark cyclopropanation reaction of styrene with ethyl diazoacetate. The results depend on the nature of the support, the chiral auxiliary, and the precursor and solvent used to carry out the cation exchange. However, the use of Cu^I or Cu^{II} is not so decisive. The best results are obtained when laponite is used as the support. The interaction with the support leads to a modification of the stereochemical course of the reaction, giving rise to an increase of the *cis*-cyclopropanes with regard to that observed in the homogeneous phase. Some of the catalysts can be recovered and reused, keeping the same catalytic activity and leading to the same enantioselectivity. © 1998 Elsevier Science Ltd. All rights reserved.

1. Introduction

The development of new heterogeneous catalysts to promote enantioselective organic reactions is a field of growing interest.[1–3] Heterogeneous catalysts are easier to handle and separate, which make them more advantageous for large-scale applications. Furthermore, in some cases, they can be recovered with only minor changes in activity and selectivity, so that they are suitable for use in continuous flow reactions.

A good number of examples of chiral heterogeneous catalysis are related to the use of metal complexes heterogenised by binding onto solid supports. In most cases, the heterogenisation is achieved through a covalent bond between the chiral auxiliary and the support. In these cases, the chiral auxiliary is modified to introduce a suitable functionality, the point by which it is grafted onto the support.

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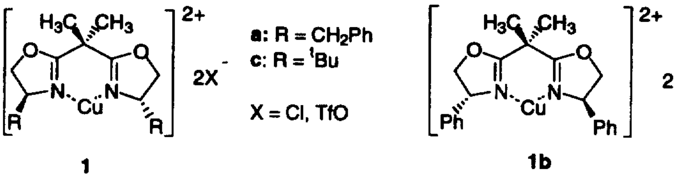
In principle, immobilisation without covalent linkage is simpler because very often it avoids the need for functionalising the complex.[1] There are several strategies of non-covalent heterogenisation. The first one involves the use of a thin layer of a suitable solvent containing the homogeneous catalyst, which is supported on a solid of high surface area.[4] The second one is the 'ship-in-a-bottle' method, namely the encapsulation within the pores of a zeolite.[5,6] Related to this is the embedding of the chiral complex into mesoporous silicates.[7] Another approach is the immobilisation of the chiral complex by occlusion in a polydimethylsiloxane membrane.[8,9] Finally, clays with cation exchange capacity can be used to support cationic complexes by electrostatic interactions with aluminosilicate sheets.[10–14] This strategy has been used in hydrogenation[15–17] and oxidation[18] reactions.

Bis(oxazolines) are among the most versatile chiral auxiliaries in enantioselective catalysis, given that their complexes with several cations promote different organic reactions.[19] These complexes are suitable candidates for heterogenisation by electrostatic interaction with anionic solids. In fact, in a previous communication[20] we have shown that bis(oxazoline)–copper complexes can be supported by cationic exchange into clays, and that the solids thus obtained are able to promote the benchmark cyclopropanation reaction between styrene and ethyl diazoacetate. In this full paper we describe the use of three different clays to support these kinds of complexes, including a full experimental description and details on the preparation and characterisation of the catalysts. The effects of the copper salt, the clay, the solvent used in the cation exchange, and the structure of the chiral auxiliary are also discussed.

2. Results and discussion

In order to compare the ability of different clays to support cationic bis(oxazoline)–copper complexes we studied the exchange of **1a**–Cu^{II} complexes (Scheme 1) into three clays with different properties: a natural smectite with lamellar structure (bentonite, >80% montmorillonite), an iron-free synthetic laponite with high swelling ability, and an acid-treated montmorillonite (K10) with disordered, house of cards, structure.[21,22]



Scheme 1.

Chiral bis(oxazoline) **1a** was obtained from dimethylmalonyl chloride and (*S*)-phenylalaninol, following the procedure described.[23,24] Its specific rotation was in agreement with previous data.[25]

In order to have reproducible starting materials, bentonite and K10 were exchanged with NaCl 1 M, washed with deionised water, and the heavy dark grey fraction was discarded. Supported catalysts were obtained by direct cation exchange of both chloride and triflate complexes. Given that cationic exchange cannot be carried out in an aqueous medium, we selected two polar solvents, namely methanol and nitroethane. The latter was tested because it has been shown that nitroalkanes have the ability to carry out cation exchange of bulky metal complexes into lamellar solids.[26] Table 1 gathers the results obtained from elemental, X-ray diffraction, and textural analyses of the clays prepared. These results show that with laponite and K10 montmorillonite the surface area is reduced when the amount of exchanged complex increases. In the case of bentonite, the starting material already has a low surface area. Both the amount of the exchanged complex and its distribution are closely related to the nature of the counterion and that of the solvent. In fact, the basal spacing of the laponite is only increased by using chloride in

Table 1
Analysis of the clays exchanged with $[\mathbf{1a}\text{–Cu}]^{2+}\ 2X^-$ complexes

Clay[a]	X^-	Solvent	Cu (mmol g^{-1})	2N/Cu	d_{001} (Å)	Surface ($m^2\ g^{-1}$)
Lap	-	-	-	-	16.0	289
Lap	Cl^-	MeOH	0.48	1.10	16.1	189
Lap	TfO^-	MeOH	0.35	1.10	17.3	207
Lap	Cl^-	$EtNO_2$	0.54	1.40	18.4	120
Lap	TfO^-	$EtNO_2$	0.21	1.30	16.2	231
Ben	-	-	-	-	14.2	30
Ben	Cl^-	$EtNO_2$	0.03	1.15	14.3	36
Ben	TfO^-	MeOH	0.16	1.20	15.7	36
K10	-	-	-	-	-	230
K10	Cl^-	$EtNO_2$	0.02	3.0	-	164
K10	TfO^-	MeOH	0.11	3.1	-	142

[a] Lap = laponite, Ben = bentonite, K10 = K10 montmorillonite.

nitroethane or triflate in methanol, whereas the latter couple is the only one that leads to an increase in the basal spacing with bentonite, and to a reasonable amount of supported complex with bentonite and K10 montmorillonite.

It is possible to speculate on the reasons for this behaviour, which depends on the equilibrium between two cations, sodium and the copper complex, and two anions, that of the copper salt and the aluminosilicate of the clay, and this equilibrium will be modified by the solvent. In this case, we work with polar solvents that have different properties. In fact, nitroethane is more dipolar and methanol is both more acidic and more basic.

The results obtained from elemental analyses show that, in laponite and bentonite, the N:Cu ratios are within the range of values expected for these complexes. In K10 montmorillonite there is an amount of nitrogen larger than expected, which indicates that the basic ligand interacts with some of the acidic sites of the clay.

We tried to obtain spectroscopic confirmation of the structure of the exchanged complexes. The diffuse reflectance UV spectra of the solids showed a band at a λ_{max} near to 730 nm, corresponding to the d–d transition of Cu^{II}, which also appears in the UV spectra of the complexes in solution.[27] However, more detailed information can be obtained from the IR spectra of the exchanged catalysts. The most significant band of the chiral ligand **1a** is that corresponding to the C=N bond, which appears at 1654 cm^{-1}. The same band is observed in the IR spectra of the complexes in solution (1661 cm^{-1} when X=Cl and 1658 cm^{-1} when X=TfO). The supported catalysts also show an intense band in the same region, irrespective of the nature of the solvent used to carry out the exchange, the counterion X, and the clay, this band appears in the range from 1639 to 1642 cm^{-1} (Fig. 1).

These solids were tested as enantioselective heterogeneous catalysts in the benchmark cyclopropanation reaction of styrene **2** with ethyl diazoacetate **3**[28] (Scheme 2).

Reactions were monitored by gas chromatography using *n*-decane as the internal standard. Asymmetric inductions were determined by chiral gas chromatography. To assign the signals to the corresponding cyclopropanes we carried out the previously described homogeneous reactions,[29] in this way we were able to determine the enantiomeric excess in both *trans*- and *cis*-cyclopropanes, and also the absolute configuration of the products.

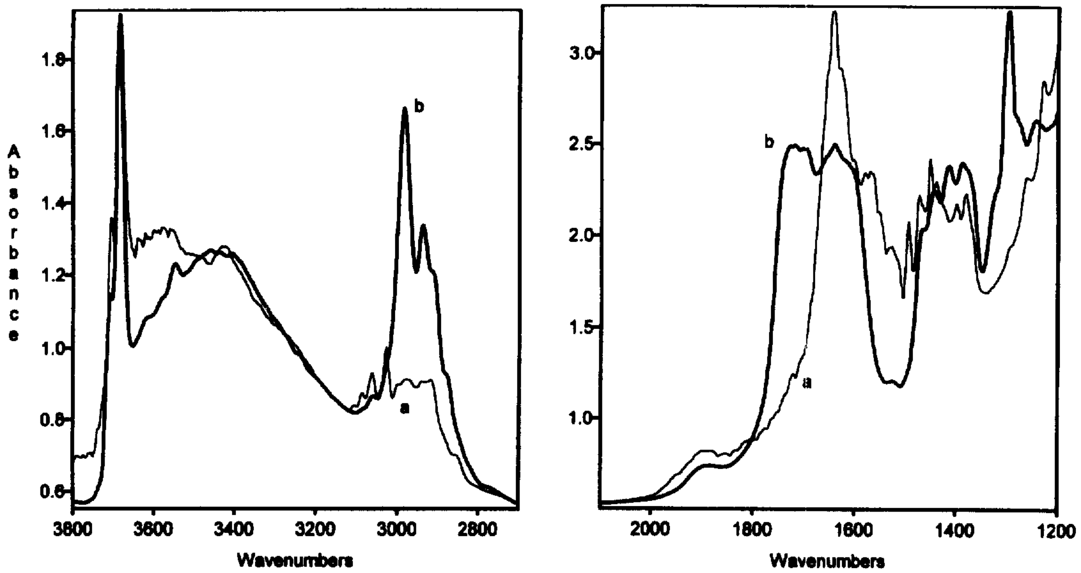
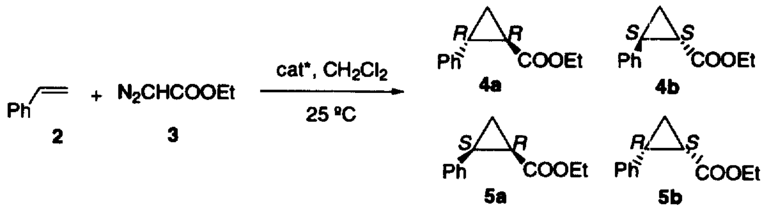


Figure 1. IR spectra of the [1a–Cu]$^{2+}$ 2Cl^{-} complex supported in laponite, using nitroethane as the cation exchange solvent, as obtained (a) and after the reaction (b)



Scheme 2.

Table 2 gathers the results obtained with the different clays. As can be seen, all the clays promote the reaction, which does not take place in the absence of a catalyst. A comparison among the laponites obtained using different counterions and different solvents shows that there are not important differences in catalytic activity. However, those solids with higher copper content and expanded basal spacing (namely those obtained using the triflate in methanol and the chloride in nitroethane) lead to higher enantioselectivities. It may be speculated that the asymmetric induction is reduced by the presence of some non-complexed Cu^{II}, leading to racemic products,[30] whose amount will depend on the cation exchange conditions. Unfortunately, the elemental analysis does not allow clarification of this point, given the intrinsic error of this technique, and the low nitrogen content of the clays. A comparison with the analogous homogeneous catalysts shows that the complexes supported in laponites lead to higher selectivities with regard to the reagents, and to higher enantioselectivities than those obtained with the chloride complex, but the use of the triflate complex improves all these results. It has been described that an increase in the basicity of the anion reduces the performance of the homogeneous catalyst. It can then be concluded that the anionic support behaves in a way intermediate between chloride and triflate.

The catalyst supported in bentonite using the triflate in methanol leads to results comparable to those obtained with the laponite prepared in the same way, which shows that the surface area of the solid is not a limiting factor.

The bentonite obtained from the chloride and the two K10 montmorillonites lead to worse results, which is mainly due to the low selectivity with regard to diazoacetate. This behaviour may be related to the low copper content of some of these catalysts, and to the nature of the support. It is important to

Table 2
Results obtained from the reaction of styrene (**2**) with ethyl diazoacetate (**3**) promoted by **1a**–Cu^{II} complexes in CH_2Cl_2 at 25°C

Clay	X^-	Solvent	t (h)	%conv.[a]	%sel. (2)[a]	%sel. (3)[a]	4:5[a]	%ee (4)[b]	%ee (5)[b]
-	Cl^-	-	13	31	26	10	2.3	4	6
-	TfO^-	-	7	69	83	58	2.1	59	53
Lap	Cl^-	MeOH	19	49	60	29	1.4	16	16
Lap	TfO^-	MeOH	22	38	66	25	1.0	24	19
Lap	Cl^-	$EtNO_2$	40	39	67	26	1.2	31	26
Lap	TfO^-	$EtNO_2$	40	45	73	33	0.9	15	10
Ben	TfO^-	MeOH	23	40	75	30	1.4	34	21
Ben	Cl^-	$EtNO_2$	22	23	73	17	1.2	18	18
K10	TfO^-	MeOH	24	20	55	11	1.2	18	17
K10	Cl^-	$EtNO_2$	120	11	49	6	1.1	30	18
Lap	TfO^-	MeOH [c,d]	22	44	73	32	1.1	14	12
Lap	Cl^-	$EtNO_2$ [c,e]	40	47	56	26	1.3	30	26
Ben	TfO^-	MeOH [c,f,g]	24	20	55	11	1.2	18	17

[a] Reaction monitored by gas chromatography. [b] Determined by gas chromatography with a chiral column; **4a** and **5a** are the major enantiomers. [c] Recovered catalysts. [d] 0.22 mmol Cu g^{-1}. [e] 0.35 mmol Cu g^{-1}. [f] 0.10 mmol Cu g^{-1}. [g] Previous to the reaction, the catalyst is treated with 0.5 mmol of **3** at 40 °C.

note that, in spite of these facts, all supported catalysts lead to asymmetric inductions better than those obtained with the chloride complex in the homogeneous phase.

A relevant fact is that the supported catalysts reduce the preference in the more stable *trans*-cyclopropanes. The same had already been observed with Cu^{II}-exchanged clays, and had been explained on the bases of the dimensionality of the clays and/or of the isolation of the catalytic sites.[30]

The three catalysts leading to the best results were recovered by filtration and washing. The recovered catalysts show a decrease in the copper content, however, the N:Cu ratio is in all cases near to the expected value. These data seem to indicate that there is leaching of some complex, however, the carbon content of the clays is not reduced to the expected extent and, in some cases, it even increases. The IR analysis of the recovered catalysts shows the C=N band at 1654 cm^{-1}, but also a new series of bands in the range 1700–1800 cm^{-1}, together with an increase in the intensity of the bands corresponding to the C–H stretching (2850–3000 cm^{-1}) (Fig. 1). These new bands show the deposition of coke, very probably polymers derived from diazoacetate, in the catalyst.

The X-ray diffraction analyses of the recovered catalysts show that both the laponite and the bentonite, exchanged from triflate, exhibit expanded basal spacing (17.7 and 15.2 Å, respectively). However, the laponite obtained from chloride loses the expanded basal spacing when recovered (15.6 Å). This value has to be taken with care, given that the diffraction line is broad and of lower intensity. This behaviour may be due to a partial destruction of the lamellar structure. In fact, the surface area increases in the recovered catalyst (175 $m^2\ g^{-1}$).

This behaviour indicates that the solvent used to carry out the cation exchange influences the structure and the stability of the clay. It may be speculated that some of this solvent remains in the environment of the copper cations, and is responsible for these differences, as it may modify the strength of the interactions between these cations and the sheets of the clay.

The recovered catalysts were tested in the same reaction (Scheme 2), and the results obtained (Table 2) show that the catalytic activity of the recovered laponites is closely similar to that of the fresh catalysts. However, only the solid obtained from chloride in nitroethane keeps the same values of enantioselectivity. The recovered bentonite has to be activated by heating with a small amount of diazoacetate. It is known that Cu^I is the active species in this reaction, and that diazoacetate reduces the Cu^{II} to Cu^I, so that the access of diazoacetate to the catalytic sites is more difficult in the recovered catalyst, which agrees with the decrease in the copper content and with the coke deposition.

In order to improve the results, we decided to obtain Cu^I catalysts. In view of the above described results, we only used laponite as the support. The cationic complexes were obtained using $CuOTf{\cdot}C_6H_6$, and the cationic exchange was efficiently carried out in nitroethane under argon atmosphere. The catalyst was tested in the benchmark reaction (Scheme 2) as obtained, stirred in dichloromethane during 30 h, or dried in the open air. Table 3 shows the results of these reactions, in comparison with those of the catalysts prepared in nitroethane from Cu^{II} complexes.

Again, the behaviour of laponite as an anion is intermediate between that of chloride and triflate. As can be seen, the supported catalyst is stable in the reaction conditions in the absence of reagents, and it is also stable in the open air. The results obtained with this catalyst are better than those obtained with its Cu^{II} analogue. However, the recovered catalyst shows a decrease in the content of copper and leads to results comparable to those obtained with the Cu^{II} catalyst prepared from chloride. It can be concluded that the Cu^I catalyst is modified during the reaction. An additional confirmation of this point is offered by the change in *trans/cis* selectivity upon recovery of this catalyst.

In order to increase the asymmetric induction we changed the chiral auxiliary. We tested two more bis(oxazolines), **1b** and **1c**, leading to better results in homogeneous reactions[28] (Scheme 1). In view of the previous work, laponite was the only clay used to support the corresponding complexes, which were obtained from $CuCl_2$ and $Cu(OTf)_2$. Chiral bis(oxazoline) **1b** was prepared from dimethyl malonyl

Table 3

Results obtained from the reaction of styrene (**2**) with ethyl diazoacetate (**3**) promoted by **1a**–Cu^I and **1a**–Cu^{II} complexes, supported in laponite by cation exchange in $EtNO_2$, in CH_2Cl_2 at 25°C

Clay	Cu	X^-	t (h)	%conv.[a]	%sel. (2)[a]	%sel. (3)[a]	4:5[a]	%ee (4)[b]	%ee (5)[b]
-	I	TfO^-	7	73	79	58	2.0	65	59
-	I	Cl^-	21	24	60	15	2.5	5	3
Lap[c]	I	TfO^-	22	36	81	29	1.6	50	35
Lap[d]	I	TfO^-	42	50	84	42	1.7	49	35
Lap[e]	I	TfO^-	40	45	79	36	1.7	51	38
Lap	II	TfO^-	40	45	73	33	0.9	15	10
Lap	II	Cl^-	40	39	67	26	1.2	31	26
Lap[f]	I	TfO^-	23	44	73	32	1.2	33	24

[a] Reaction monitored by gas chromatography. [b] Determined by gas chromatography with a chiral column; **4a** and **5a** are the major enantiomers. [c] 0.37 mmol Cu g^{-1}, 2N/Cu = 1.2. [d] Catalyst stirred for 30 h in CH_2Cl_2 under argon. [e] Catalyst dried in the open air. [f] Recovered catalyst, 0.20 mmol Cu g^{-1}, 2N/Cu = 1.2.

Table 4
Analysis of the laponites exchanged with **1b** and [**1c**–Cu]$^{2+}$ 2X$^-$ complexes

Chiral auxiliary	X$^-$	Solvent	Cu (mmol g^{-1})	2N/Cu	d_{001} (Å)
1b	Cl$^-$	EtNO$_2$	0.37	1.15	17.8
1b	Cl$^-$	MeOH	0.60	0.50	16.7
1b	TfO$^-$	MeOH	0.28	1.20	17.7
1c	Cl$^-$	EtNO$_2$	0.11	1.30	15,6 (broad)

chloride and (*R*)-phenylglycinol, using the method previously described.[23–25] Chiral bis(oxazoline) **1c** was purchased from Aldrich.

The results obtained using **1b** as the chiral auxiliary indicate that once again, the laponites exchanged using copper chloride in nitroethane and copper triflate in methanol show expanded basal spacing (Table 4). However, when the chloride of the **1c**–Cu^{II} complex is exchanged using nitroethane, the resulting material shows a broad diffraction line of low intensity. With this bulkier chiral auxiliary, the complex cannot be accommodated into the interlamellar space, and its exchange originates a partial destruction of the lamellar structure. Again, the N:Cu ratios agree, within the limits of experimental error, with the expected value. However, when the [**1b**–Cu]$^{2+}$ 2Cl$^-$ complex is exchanged in nitroethane, the value of this ratio is near 1, i.e., about 50% of the exchanged copper is not complexed (Table 4).

The clays were analysed by IR spectroscopy, showing the expected C=N band between 1650–1660 cm^{-1}, which indicates the presence of the chiral ligand.

These clays were tested as catalysts in the reaction of styrene with ethyl diazoacetate, and the results obtained are gathered in Table 5. Again, all solids promote the reaction with a behaviour intermediate between the homogeneous chloride and triflate catalysts, and with a greater proportion of the less stable *cis*-cyclopropanes. The catalyst obtained from **1c** yields the higher enantioselectivities, but both the catalytic activity and the enantioselectivity are noticeably reduced in the reaction promoted by the recovered catalyst. With this bulky chiral auxiliary the interaction of the complex with the support, and/or that of the ligand with the copper, may be weaker, and part of the ligand may be lost. Both the copper analysis of the recovered catalyst and the activity agree with the latter hypothesis. In order to obtain further confirmation of this fact, to the solution obtained after separation of the solid catalyst in the first reaction, additional amounts of reagents were added, with no increase in the amount of cyclopropanes being observed. In fact, the reaction conditions are not exactly the same, however, this experiment suggests that the leaching of Cu^{II} does not occur or it is very low. It can be concluded that the lower enantioselectivity obtained with the recovered catalyst is due to the leaching of the chiral ligand, so that part of the reaction is promoted by non-complexed copper, and leads to the racemic product.[30]

The clay obtained from the cationic exchange of [**1b**–Cu]$^{2+}$ 2Cl$^-$, carried out in methanol, leads to very low enantioselectivities, in agreement with the low nitrogen content and the presence of non-chiral catalytic centres.

The catalysts obtained by exchange of [**1b**–Cu]$^{2+}$ 2Cl$^-$ in nitroethane and of [**1b**–Cu]$^{2+}$ 2Cl$^-$ in methanol lead to similar results. Surprisingly, they afford a reasonable asymmetric induction in *trans*-cyclopropanes, but very low percentages of enantiomeric excess are obtained for the *cis*-cyclopropanes. It is very difficult to find an explanation for this behaviour, which is peculiar to this supported catalyst. In fact, all the rest of the catalysts, both homogeneous and heterogeneous, tested in this work lead to only a slightly lower asymmetric induction in the *cis*-cyclopropanes with regard to the *trans*-cyclopropanes. What is clearly shown by this result is that the support is not a mere spectator of the reaction, and that the

Table 5
Results obtained from the reaction of styrene (**2**) with ethyl diazoacetate (**3**) promoted by **1b**–Cu^{II} and **1c**–Cu^{II} complexes, supported in laponite, in CH_2Cl_2 at 25°C

Chiral auxiliary	X$^-$	Solvent	t (h)	%conv.[a]	%sel. (2)[a]	%sel. (3)[a]	4:5[a]	%ee (4)[b]	%ee (5)[b]
1b	Cl$^-$	MeOH	23	55	76	42	1.5	7	0
1b	Cl$^-$	$EtNO_2$	22	44	60	27	0.9	46	3
1b	TfO$^-$	MeOH	21	40	76	31	1.2	43	6
1b[c]	TfO$^-$	MeOH	24	38	74	28	1.2	41	13
1c	Cl$^-$	$EtNO_2$	39	37	82	30	1.8	69	64
1c[d]	Cl$^-$	$EtNO_2$	88	22	59	26	1.4	43	37
1c[e]	Cl$^-$	-	21	33	74	24	2.3	2	7
1c[e]	TfO$^-$	-	7	81	75	61	2.4	91	88

[a] Reaction monitored by gas chromatography. [b] Determined by gas chromatography with a chiral column; **4b** and **5b** are the major enantiomers with **1b**, and **4a** and **5a** with **1c**. [c] Recovered catalyst, 0.25 mmol Cu g^{-1}, 2N/Cu = 1.2, d_{001} = 17.7 Å. [d] Recovered catalyst, 0.10 mmol Cu g^{-1} [e] Homogeneous reaction.

interaction with the support modifies the relative energies of the four diastereomeric transition structures leading to the four diastereomeric products. This conclusion is also in agreement with the changes in *trans/cis* selectivity induced by the support.

The catalyst leading to the best results was recovered by filtration and washing, and shows neither a significant leaching of copper, nor a decrease of the basal spacing. In agreement with these facts, the recovered and the freshly prepared catalysts lead to almost the same results. This is probably the most stable catalyst described in this work, and therefore the catalyst with the stronger complex–support interaction, which agrees with the unexpected stereochemical course of the reaction.

3. Conclusions

Chiral bis(oxazolines)–copper complexes can be supported by cation exchange into clays. The structural, textural and catalytic properties of the solids obtained strongly depend on the counterion of the cationic complex and on the solvent used to carry out the cation exchange.

Laponite is the support leading to the best catalytic performances, which are intermediate between those observed in the homogeneous phase for the chloride and triflate complexes. The size of the complex also influences the exchange process, so that the clay loses a part of its lamellar structure.

All the catalysts can be recovered, but, in general, leaching of complex and a loss of catalytic activity and enantioselectivity are observed. Two of the laponites, namely those obtained from [**1a**–Cu]$^{2+}$ 2Cl^{-} in nitroethane, and particularly, from [**1b**–Cu]$^{2+}$ 2TfO^{-} in methanol, lead to the same results when freshly prepared as well as recovered. A stronger complex–support interaction may be the origin of this stability.

Triflate Cu^{I} complexes can also be supported using nitroethane as the cation exchange solvent. The solids thus obtained are stable in solution and in the open air, and they lead to results that are somewhat better than those afforded by their Cu^{II} analogues. However, the catalysts recovered after the reaction do not show noticeable differences with the Cu^{II} catalysts.

The interaction with the support modifies the relative energies of the four diastereomeric transition states leading to the products. Consequently, both the *trans/cis* selectivity and the enantioselectivities are modified. Furthermore, the enantioselectivities in *trans*- and *cis*-cyclopropanes can be very different, as shown in the case of the **1b**–Cu complexes supported in laponite from different precursors and using different solvents.

4. Experimental

2,2′-Isopropylidene[(4*S*)-4-benzyl-2-oxazoline] **1a** and 2,2′-isopropylidene[(4*R*)-4-phenyl-2-oxazoline] **1b** were obtained from (*S*)-phenylalaninol and (*R*)-phenylglycinol, respectively, as previously described.[21,22] 2,2′-Isopropylidene[(4*S*)-4-*tert*-butyl-2-oxazoline] was purchased from Aldrich.

4.1. Preparation of the exchanged catalyst

To a solution of the bis(oxazoline) **1** (1 mmol) in methanol or nitroethane (2 ml), 1 mmol of $CuCl_2 \cdot 2H_2O$ or $Cu(TfO)_2$ is added. When the complexes with $CuCl_2$ are used in methanol, the amount of solvent has to be increased to 170 ml. In general, the complexes formed from $CuCl_2$ are green, whereas those obtained from $Cu(TfO)_2$ are blue.

To this solution 1 g of the corresponding clay (Na-bentonite, Na-K10 or laponite) is slowly added, and the resulting suspension is stirred for 24 h. The solid is filtered, washed with the same solvent (methanol or nitroethane), and then with dichloromethane, and dried under air before use.

The same method is used to exchange the complex of **1a** with CuTfO in laponite using nitroethane. However, the preparation and subsequent drying of the catalyst are carried out under an argon atmosphere.

4.2. Characterisation of the catalyst

Copper analyses were carried out by plasma emission spectroscopy on a Perkin–Elmer Plasma 40 emission spectrometer. Carbon and nitrogen analyses were carried out in a Perkin–Elmer 2400 elemental analyser. Step-scanned X-ray diffraction patterns of oriented samples were collected at room temperature from 3° in 2θ up to 60°, using a D-max Rigaku system with rotating anode. The diffractometer was operated at 40 kV and 80 mA, and the Cu Kα radiation was selected using a graphite monochromator. Diffuse reflectance UV spectra were recorded with an Unicam UV4 spectrometer equipped with a Labsphere diffuse reflectance attachment. IR spectra were taken from self-supporting wafers of the catalyst samples, treated under high vacuum ($<10^{-5}$ torr) at 50°C for 2 h, with a Mattson Genesis Series FTIR.

4.3. Cyclopropanation reactions with homogeneous catalysts

Under argon, to a solution of the bis(oxazoline) **1** (0.25 mmol) in dichloromethane (10 ml), 0.25 mmol of the copper salt is added, and the mixture is stirred for 15 min. After this time, styrene (2.5 mmol) and *n*-decane (500 mg), dissolved in 15 ml of the same solvent, are added, and ethyl diazoacetate (1.25 mmol) is added during 2 h with a syringe pump. The reaction is monitored by gas chromatography, and after the consumption of the diazoacetate, a second portion of this reagent is added in the same way. When $CuCl_2$ is used, the solution of the complex is heated at 40°C for some minutes with a few drops of ethyl diazoacetate, prior to the styrene addition.

The results of the reactions were determined by gas chromatography, FID from Hewlett Packard 5890II; cross-linked methyl silicone column: 25 m×0.2 mm×0.33 μm; helium as carrier gas, 20 p.s.i.; injector temperature: 230°C; detector temperature: 250°C; oven temperature program: 70°C (3 min), heat at 15°C min^{-1} to 200°C (5 min); retention times: ethyl diazoacetate **3** 4.28 min, styrene **2** 5.03 min, *n*-decane 6.93 min, diethyl fumarate 8.73 min, diethyl maleate 9.04 min, *cis*-cyclopropanes **5** 11.84 min, *trans*-cyclopropanes **4** 12.35 min.

The asymmetric inductions of the reactions were also determined by gas chromatography, FID from Hewlett Packard 5890II, Cyclodex B column: 30 m×0.25 mm×0.25 μm; helium as carrier gas, 20 p.s.i.; injector temperature: 230°C; detector temperature: 250°C; oven temperature program: 125°C isothermal; retention times: (1*S*,2*R*)-cyclopropane **5b** 28.9 min, (1*R*,2*S*)-cyclopropane **5a** 29.8 min, (1*R*,2*R*)-cyclopropane **4a** 34.3 min, (1*S*,2*S*)-cyclopropane **4b** 34.9 min. The peaks were assigned to the corresponding enantiomers by comparison with previously described results. The *cis* and *trans* stereochemistry was assigned by comparison of the peak ratios with those obtained with the non-chiral column.

4.4. Cyclopropanation reactions with heterogeneous catalysts

Under argon, to a suspension of the catalyst (150 mg) in dichloromethane (5 ml) with *n*-decane (100 mg) and styrene (5 mmol), ethyl diazoacetate (2.5 mmol) in dichloromethane (0.5 ml) is added during 2 h with a syringe pump. The reaction is monitored by gas chromatography, and after the consumption of the diazoacetate, a second portion of this reagent is added in the same way. In some cases (see Table 2) the catalyst is heated at 40°C for some minutes with a small amount of diazoacetate. After the reaction, the catalyst is filtered off, washed with dichloromethane, and dried in the open air (the clays obtained from Cu^I complexes are dried under argon). The recovered catalysts are reused, following the same method.

The results of the reactions are determined by gas chromatography, as described above.

The cyclopropanes were purified by column chromatography on silica gel, using *n*-hexane:ethyl acetate (40:1) as an eluent, and their structures confirmed by ^{1}H NMR.

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