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Surface-mediated improvement of enantioselectivity with clay-immobilized copper catalysts

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Abstract

The clay surface plays a role in the enantioselectivity of the cyclopropanation reaction, in the case of copper catalysts immobilized on laponite by electrostatic interactions. The effect is different depending on the type of chiral ligand, bis(oxazoline) or pyridineoxazoline. In the first case the clay promotes a reversal of the stereochemical course of the reaction. The pyridineoxazoline-copper complexes lead to very low enantioselectivity in homogeneous phase. However, the asymmetric induction increases when the complexes are immobilized on laponite, showing that it is possible to design good chiral ligands specific for the use in immobilized catalysts.

Keywords: Asymmetric catalysis; Clays; Immobilization; Solvent effects; Supported catalysts

1. Introduction

The development of enantioselective heterogeneous catalysts is a field of growing interest due to the advantages of heterogeneous over homogeneous catalysts in large scale application [1]. One of the most frequently used strategies to prepare chiral heterogeneous catalysts is the immobilization of chiral homogeneous complexes [2]. In most cases the catalyst is obtained by covalent bonding of the chiral ligand to an insoluble support, and both the support and the immobilization method decisively influence the catalytic activity and the enantioselectivity [3–5]. A clear example is the covalent immobilization of chiral bis(oxazoline) ligands [6–9], whose efficiency depends on the nature of the support, its morphology, the spacer and the number of bonds between ligand and support [10–18].

The reasons for the influence on the enantioselectivity are not clearly understood, but in some cases they have been explained by the necessary modification of the chiral ligand to allow its covalent bond to the support. In other cases the support morphology is decisive, which may be related to its effect on the environment of the catalytic centers.

In order to avoid the chemical modification of the chiral ligand, the immobilization without covalent bond formation has been explored in some cases [2]. In this regard, cationic bis(oxazoline)-copper complexes have been immobilized by electrostatic interactions onto anionic supports [19–24]. However,

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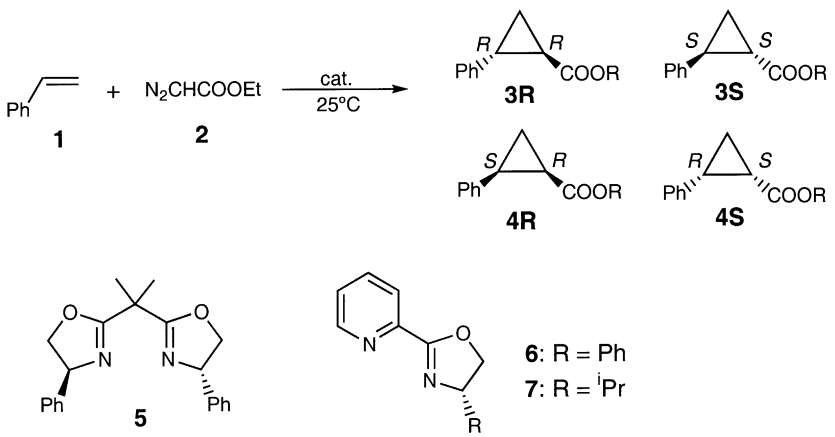

Scheme 1. Cyclopropanation reaction of styrene with ethyl diazoacetate and ligands used in this work.

it has been shown that even with this approach the influence of the support cannot be avoided. This influence is due, on the one hand, to the fact that the solid counter-ion has not the same coordinating properties as those used in homogeneous phase [19]. Furthermore, the steric interaction between the support and the different transition states may play a decisive role in the enantioselectivity of the reaction.

All these problems are related with the general idea of "immobilization of chiral catalysts leading to high enantioselectivity in homogeneous phase". As we are conscious of the possible (negative) influence of the immobilization, we normally try to reduce it by support modification, support–catalyst separation or design of new immobilization strategies. In any case, we are implicitly assuming a non-necessarily correct statement: "the best homogeneous catalyst will remain the best upon immobilization". This approach works in some cases, but in some others it leads to deceiving results, because an excellent homogeneous catalyst is converted into a bad immobilized one. A more difficult, but probably better, approach is to design a catalyst specifically for solid phase, because the same effect that leads to bad results after immobilization of a good homogeneous catalyst would be able to improve a bad homogeneous catalyst upon immobilization.

In this paper we try to illustrate this novel concept in the case of clay-immobilized cationic copper complexes, used as catalysts in the benchmark cyclopropanation of styrene and ethyl diazoacetate [25] (Scheme 1).

2. Results and discussion

During our work on immobilization of bis(oxazoline)-copper complexes onto clays [26,27], we observed an effect of the solvent on the stereochemical course of the cyclopropanation reaction. Thus, in the reaction catalyzed by the complex **5**-Cu(II), both the *trans*/*cis* ratio and the enantioselectivity were modified by the use of a solvent of low dielectric constant (Table 1). These results were rationalized on the basis of an increased steric interaction of the clay with the Cu-carbene intermediate and with the incoming styrene [28], taking into account that this step determines the stereochemical result of the reaction [29].

Table 1
Results of the cyclopropanation reaction between styrene (**1**) with ethyl diazoacetate (**2**) catalyzed by **5**-Cu complexes[a]

Counter-ion	Solvent	Yield (%)[b]	*trans*/*cis*[b]	% ee[c]	
				trans	*cis*
TfO[d]	CH_2Cl_2	33	71/29	54 (**3***R*)	42 (**4***R*)
TfO[d]	Styrene	41	69/31	55 (**3***R*)	42 (**4***R*)
Laponite	CH_2Cl_2	28	61/39	49 (**3***R*)	24 (**4***R*)
Laponite	Styrene	40	31/69	7 (**3***R*)	34 (**4***S*)
Laponite	*n*-C_6H_{14}[e]	10	31/69	3 (**3***R*)	33 (**4***S*)

[a] Data from [27].
[b] Determined by GC. Total conversion of ethyl diazoacetate.
[c] Determined by GC with a Cyclodex-B column. Major product in parentheses.
[d] Homogeneous reactions.
[e] Reaction carried out under reflux.

These results are interesting because they demonstrate a previously unknown role of the catalyst surface, although the effect was a lower enantioselectivity. However, a new question arises: is it possible to design a catalyst where the surface had a positive effect on the enantioselectivity?

With catalyst **5**-Cu the stereochemistry of the cyclopropanation depends on all the possible steric interactions between the incoming styrene, the ester group of diazoacetate, the phenyl group of the chiral ligand and finally the clay surface (Fig. 1). However, the influence of the surface is limited by the presence of two phenyl groups in the chiral ligand, which are necessary to keep the C_2-symmetry and to obtain high enantioselectivity in homogeneous phase. One can speculate that the elimination of one of those phenyl groups would favor the approach of the complex to the clay surface, increasing in that way the influence of the solid on the stereochemistry of the process.

Probably one of the most simple ways to obtain a bidentate ligand with a related structure is the synthesis of pyridineoxazolines (**6** and **7**). They were obtained from picolinic acid and the corresponding aminoalcohol in three steps, because in our hands this method led to better yields than the reported one-pot synthesis [30]. Solid catalysts were obtained by cationic exchange of the ligand-Cu$(OTf)_2$ complex in methanol with the sodium form of laponite. In contrast with the bis(oxazoline)-based catalysts, some preliminary cyclopropanation experiments showed partial leaching of active species from the clay. This can be due to the presence of physisorbed or only partially exchanged complex, i.e. substitution of only one triflate anion by a negative charge of the clay surface. In such a case,

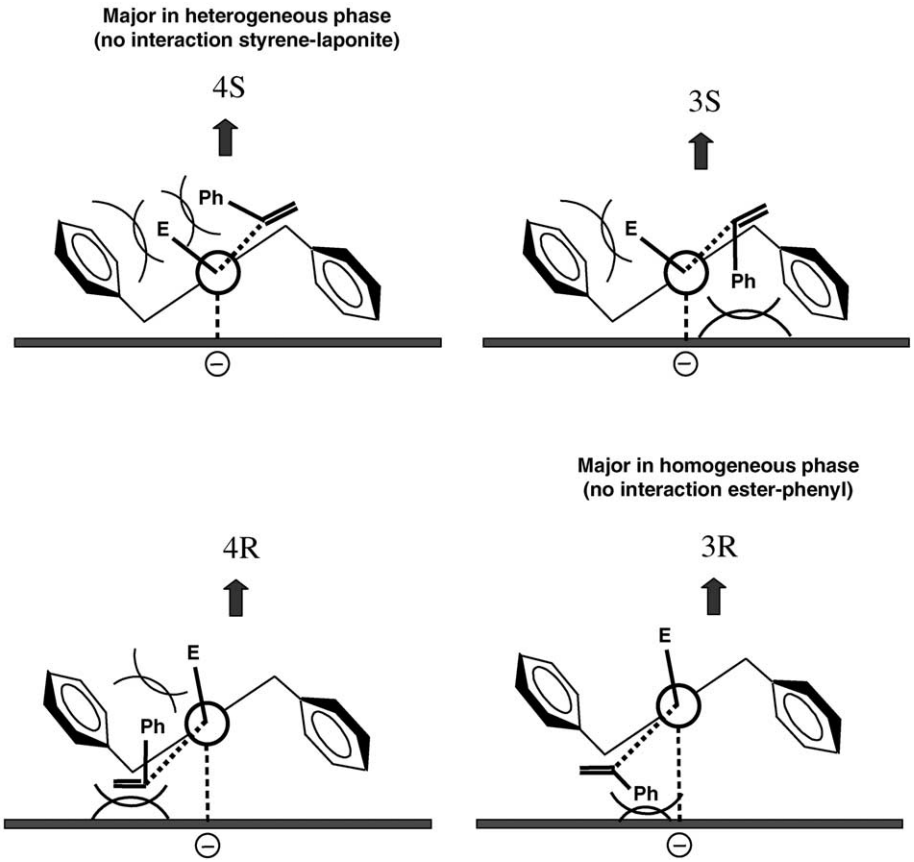

Fig. 1. Steric interactions in the possible approaches of styrene to the copper-carbene intermediate in the laponite-immobilized **5**-Cu catalyst.

the reduction of Cu(II) to Cu(I) by ethyl diazoacetate would produce a soluble ligand-CuOTf. Because of this, the solids were treated with an excess of diazoacetate in order to eliminate all this "non-properly" exchanged complex. Solids were characterized by different techniques. The copper analysis (Table 2) shows that the amount of exchanged complex is similar to that obtained with bis(oxazoline)-copper complexes in similar conditions [27]. As in those cases, the clays containing chiral complex show reduced surface area and increased basal spacing (Table 2). IR spectra of the freshly exchanged solids (Fig. 2b) confirm the integrity of the complex with the presence of the typical bands of the ligand (Fig. 2a) at 1652 cm^{-1} (C=N) and 1596 cm^{-1} (C–C in pyridine). In the case of the samples treated with ethyl diazoacetate (Fig. 2c) it is clear the presence of products from the dimerization reaction, demonstrated by the carbonyl band at 1743 cm^{-1}.

The homogeneous and heterogeneous catalysts were tested in the above mentioned cyclopropanation reaction and the results are gathered in Table 3. As expected, the homogeneous catalysts are active but poorly enantioselective. In the case of bis(oxazoline) ligands (Fig. 1), the enantioselectivity is explained by the interaction of the ester group from diazoacetate with the substituent in the oxazoline ring in the transition states leading to the minor *cis*- and *trans*-products

Table 2
Laponites prepared by cationic exchange with pyridineoxazoline-Cu complexes

Ligand	Treatment	mmol Cu/g	d_{001} (Å)	Surface area ($m^2\,g^{-1}$)
–[a]	Freshly exchanged	0.72	13.8	290
6	Freshly exchanged[b]	0.31	17.9	215
	Diazoacetate[c]	0.25	17.9	–
	Cyclopropanation[d]	0.23	18.0	–
7	Freshly exchanged[b]	0.24	16.3	228
	Diazoacetate[c]	0.19	16.9	–
	Cyclopropanation[d]	0.18	17.7	–

[a] Cu(II)-laponite prepared by exchange with $CuCl_2$ in water.
[b] After exchange with pyridineoxazoline-Cu$(OTf)_2$ in methanol, filtration, washing and drying.
[c] Treatment with an excess of ethyl diazoacetate in dichloromethane at room temperature, filtration, Soxhlet extraction and drying.
[d] After one cyclopropanation reaction in styrene as a solvent.

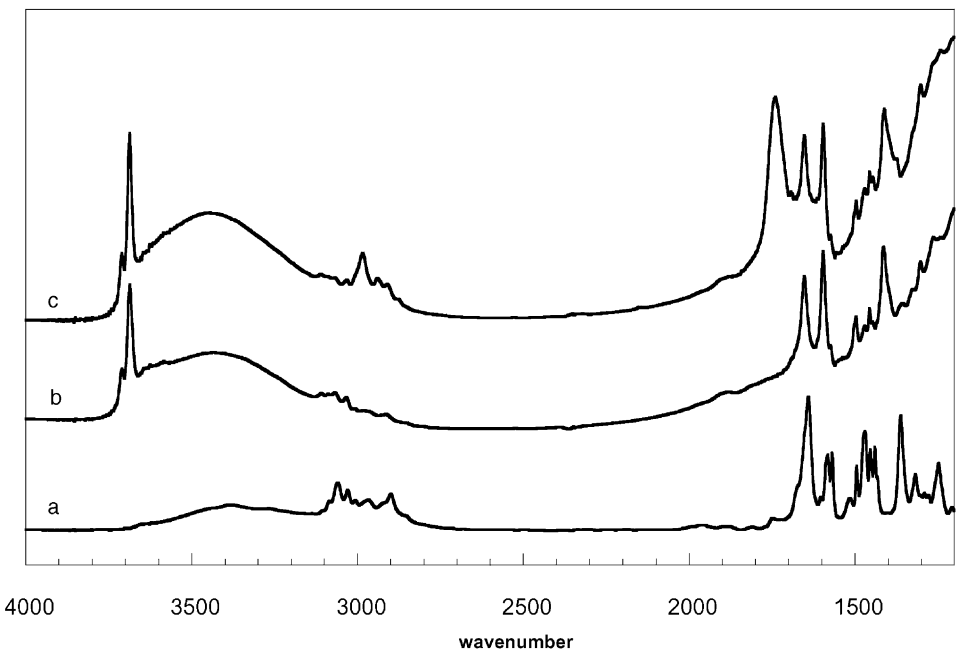

Fig. 2. IR spectra: (a) ligand **6**; (b) freshly exchanged laponite-immobilized **6**-Cu complex; (c) laponite-immobilized **6**-Cu complex treated with ethyl diazoacetate.

Table 3
Results of the cyclopropanation reaction between styrene (**1**) and ethyl diazoacetate (**2**) catalyzed by pyridineoxazoline-Cu complexes

Ligand	Counter-ion	Solvent	Yield (%)[a]	*trans*/*cis*[a]	% ee[b]	
					trans	*cis*
6	TfO[c]	CH_2Cl_2	65	67/33	5 (**3***R*)	17 (**4***R*)
	Laponite[d]	CH_2Cl_2	59	45/55	27 (**3***R*)	27 (**4***R*)
	Laponite[d]	Styrene	68	31/69	65 (**3***R*)	24 (**4***R*)
7	TfO[c]	CH_2Cl_2	55	69/31	4 (**3***R*)	8 (**4***R*)
	Laponite[d]	CH_2Cl_2	48	46/54	13 (**3***R*)	1 (**4***S*)
	Laponite[d]	Styrene	53	33/67	27 (**3***R*)	12 (**4***S*)

[a] Determined by GC. Total conversion of ethyl diazoacetate.
[b] Determined by GC with a Cyclodex-B column. Major product in parentheses.
[c] Homogeneous reactions.
[d] Sample treated previously with an excess of ethyl diazoacetate.

[29]. Due to the C_2-symmetry of the ligand, the ester group is always *syn* with respect to one substituent. However, in pyridineoxazolines one possible Cu-carbene intermediate presents the ester and the oxazoline substituent in an *anti* disposition (Fig. 3). The absence of any ester–substituent interaction in the corresponding transition states coming from this intermediate allows to speculate that this would be the most reactive but leading to no enantioselectivity.

When the complex **6**-Cu is immobilized on laponite, the enantioselectivity increases. It may be speculated that the interaction between the clay surface and the groups of the above mentioned *anti* intermediate should favor the *syn* intermediate. In that case the enantioselection mechanism would act as in the case of bis(oxazoline) ligands. The values of enantiomeric excess, lower than those obtained with ligand **5**, must be due to the difference in chelate size. In fact, it has been described [25] that six-membered chelates, as in bis(oxazolines), lead to much better enantioselectivities than five-membered ones, which is the case of pyridineoxazolines. Even seven-membered chelates have shown better performance in some cases [31]. However, the results demonstrate that, on the clay, the C_1-symmetric ligand behaves as a C_2-symmetric one because of the surface influence.

On the other hand, the *trans*/*cis*-selectivity in homogeneous phase is a consequence of the interaction between the ester group and the phenyl group of the incoming styrene in the transition state leading to the *cis*-products. On the clay, the *trans*-approach is disfavored by the interaction of the phenyl group of the styrene with the surface, which accounts for the increase in the amount of *cis*-cyclopropanes. This seems to be a general feature of the clay-supported copper catalysts, which seems to be very difficult in solution, given that there is only one example described in the literature about *cis*-preference with homogeneous copper catalysts using non-conventional bis(oxazolines) [32].

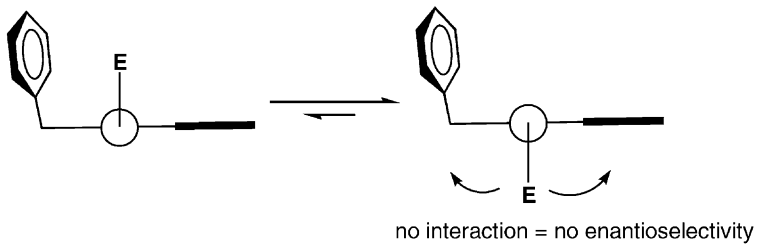

Fig. 3. Possible **6**-Cu-carbene intermediate complexes in solution.

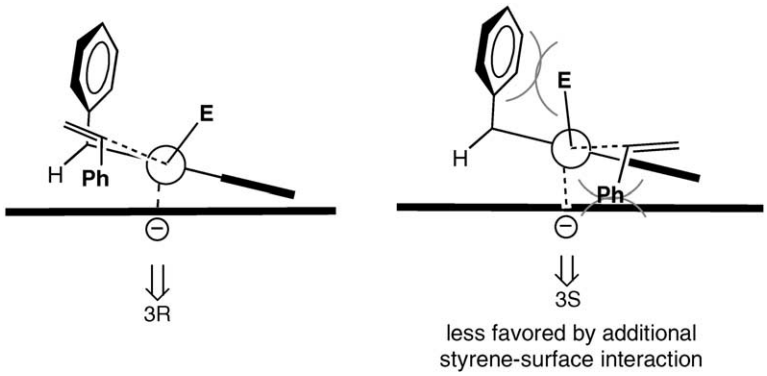

Fig. 4. Models for asymmetric induction with laponite-immobilized **6**-Cu complex.

We have shown that the use of a solvent with a lower dielectric constant increases the electrostatic interaction between the anionic surface of the clay and the cationic catalyst, in such way that they approach each other and the steric influence of the surface increases [28]. In the case of ligand **6**, the use of styrene as both reagent and solvent leads to an increase in the *cis*-preference, as expected for a catalyst closer to the clay surface. Under that condition, the enantioselectivity for *cis*-cyclopropanes is not modified, but it noticeably increases for *trans*-products, showing that the influence of the surface is much more important in the transitions states leading to the *trans*-cyclopropanes. It seems evident that the disposition of the intermediate with the ester group far from the surface induces the *trans*-approach to place the styrene phenyl group near to the surface. Taking this fact into account, the following model (Fig. 4) affords a speculative interpretation of the results. The chiral ligand presents a planar and a tetrahedral components, the pyridine and oxazoline groups, respectively. Due to steric reasons, the planar group may be closer to the surface, with the intermediate forming a certain angle with the surface. In this disposition, the approach leading to **3***S* will be disfavored not only by the ester–oxazoline substituent interaction, but also by a stronger interaction with the surface of the solid.

It is difficult to find an explanation for the slight **4***S* preference in the reactions promoted by the immobilized **7**-Cu complex. However, the reaction in styrene shows the same tendency to increase the *cis*/*trans* ratio and the **3***R* preference, in agreement with the proposed model.

3. Experimental

^{1}H NMR spectra were recorded on Varian 200 MHz with TMS as internal standard. Chemical shifts are reported in ppm, and coupling constants in Hz. All the reactions were carried out under an atmosphere of dry nitrogen using flame dried glassware and freshly distilled dry solvents.

3.1. Synthesis of the pyridineoxazolines

To a solution of picolinic acid (2.0 g, 16.25 mmol) in chlorobenzene (50 ml), thionyl chloride (16 ml, 0.22 mol) was added dropwise. The solution was heated under reflux for 1 h. After cooling, the solvent and the excess of $SOCl_2$ were eliminated under reduced pressure to obtain picolinoyl chloride in quantitative yield.

To a solution of (*S*)-valinol (1.83 g, 17.8 mmol) and triethylamine (4.4 ml, 34.1 mmol) in dichloromethane (50 ml) at 0 °C, a solution of picolinoyl chloride (2.3 g, 16.25 mmol) in dichloromethane (50 ml) was added dropwise. The resulting solution was stirred at room temperature for 24 h, washed with saturated $NaHCO_3$ aqueous solution (3× 50 ml) and dried with $MgSO_4$. The solvent was eliminated under reduced pressure to obtain *N*-[1-(*S*)-isopropyl-2-hydroxyethyl]pyridine-2-carboxamide. To a solution of this amide in toluene

(50 ml) at room temperature, thionyl chloride (16 ml) was added dropwise. The solution was heated under reflux for 1.5 h. After cooling, the solvent and the excess of $SOCl_2$ were eliminated under reduced pressure to obtain a brown oil, which was purified by column chromatography on silica (hexanes/ethyl acetate = 6/4). *N*-[2-Chloro-1-(*S*)-isopropylethyl]pyridine-2-carboxamide (1.84 g, 50% yield from picolinic acid) was obtained as a white solid.

To a solution of sodium hydride (633 mg, 27.5 mmol) in THF (100 ml) at 0 °C, *N*-[2-chloro-1-(*S*)-isopropylethyl]pyridine-2-carboxamide (1.81 g, 8 mmol) was added and the mixture was stirred at 0 °C for 1.5 h. The solid was filtered off, the filtrate was concentrated under vacuum, dissolved in dichloromethane (25 ml), washed with brine (3× 20 ml) and dried with $MgSO_4$. After solvent evaporation the crude oil was crystallized from hexanes/ethyl acetate to obtain 2-[(*S*)-4-isopropyloxazolin-2-yl]pyridine (**7**) (1.14 g, 75% yield). ^{1}H NMR ($CDCl_3$): 8.67 (m, 1H), 8.02 (d, 1H, $J = 7.0$), 7.74 (dt, 1H, $J = 7.7$ and 1.5), 7.35 (m, 1H), 4.47 (m, 1H), 4.13 (m, 2H), 1.87 (m, 1H), 1.03 (d, 3H, $J = 7.0$), 0.91 (d, 3H, $J = 7.0$).

2-[(*S*)-4-Phenyloxazolin-2-yl]pyridine (**6**) was obtained in a similar way. ^{1}H NMR ($CDCl_3$): 8.64 (m, 1H), 8.07 (d, 1H, $J = 8.1$), 7.69 (dt, 1H, $J = 7.7$, and 1.8), 7.33 (m, 1H), 7.25–7.10 (m, 5H), 5.37 (dd, 1H, $J = 10.3$ and 8.4), 4.80 (dd, 1H, $J = 10.3$ and 8.8), 4.29 (t, 1H, $J = 8.7$).

3.2. Preparation of the immobilized catalysts

The complex for cationic exchange was prepared by mixing $Cu(OTf)_2$ (202 mg, 0.56 mmol) with a solution of pyridineoxazoline (0.56 mmol) in dichloromethane (1.2 ml). After stirring for 15 min, the solution was filtered through a syringe microfilter and the solvent was evaporated under reduced pressure. The residue was re-dissolved in methanol (7 ml) and laponite (700 mg) was added to this solution. The suspension was stirred at room temperature for 24 h, the solid was filtered and thoroughly washed with methanol and dichloromethane. The resulting freshly exchanged catalyst was dried under vacuum overnight.

To a suspension of the freshly exchanged catalyst (555 mg) in dichloromethane (16 ml) at room temperature, a solution of ethyl diazoacetate (1.05 g, 9.25 mmol) in dichloromethane (5 ml) was added dropwise. The suspension was stirred at room temperature for 18 h, the solid was filtered, washed with dichloromethane in a Soxhlet apparatus (3 days) and finally dried under vacuum.

The catalysts were characterized by elemental analysis (Perkin-Elmer 240 elemental analyzer), copper analysis (Perkin-Elmer Plasma 40 emission spectrophotometer), step-scanned X-ray diffraction patterns of oriented samples (D-max Rigaku system with a rotating anode), transmission FT-IR spectroscopy of self-supported wafers evacuated ($<10^{-4}$ Torr) at 50 °C (Mattson Genesis Series) and N_2 adsorption (BET, Micromeritics ASAP 2000).

3.3. Cyclopropanation reactions

Ethyl diazoacetate (580 mg, 5 mmol) was slowly added with a syringe pump to a suspension of laponite catalyst (150 mg) in styrene (16 ml or 520 mg in 15 ml methylene chloride) containing *n*-decane (internal standard, 150 mg) at room temperature. The reaction was monitored by gas chromatography with DB-1 and Cyclodex-B columns [19]. After total consumption of the diazoacetate the solid catalyst was filtered off, washed with methylene chloride and air-dried.

4. Conclusions

The results described in this paper, although not excellent from a synthetic point of view, provide a clear confirmation to the previous hypothesis about the crucial influence of the clay surface on the stereochemical course of the cyclopropanation catalyzed by cationic copper complexes immobilized by electrostatic interactions. Taking this into account, it is important to understand these effects in order to design ligands specifically suitable for their use in heterogeneous systems. It has been demonstrated that with pyridineoxazolines it is possible under heterogeneous conditions to obtain better enantioselectivities than in homogeneous phase. It is specially remarkable the increase from 5 to 65% ee in the case of ligand **6**. In the case of bis(oxazolines) it is even possible to favor the reversal of the stereochemical course, a much more difficult task in homogeneous phase. These results open the way to the design of efficient chiral ligands,

specifically for immobilization through electrostatic interactions.

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References

[1] H.-U. Blaser, B. Pugin, in: G. Jannes, V. Dubois (Eds.), Chiral Reactions in Heterogeneous Catalysis, Plenum Press, New York, 1995, pp. 33–57.
[2] D.E. De Vos, I.F.J. Vankelecom, P.A. Jacobs (Eds.), Chiral Catalysts Immobilization and Recycling, Wiley–VCH, Weinheim, 2000.
[3] D.W.L. Sung, P. Hodge, P.W. Startford, J. Chem. Soc., Perkin Trans. 1 (1999) 1463.
[4] B. Altava, M.I. Burguete, J.M. Fraile, J.I. García, S.V. Luis, J.A. Mayoral, M.J. Vicent, Angew. Chem. Int. Ed. Engl. 39 (2000) 1503.
[5] E. Breysse, C. Pinel, M. Lemaire, Tetrahedron: Asymmetry 9 (1998) 897.
[6] A.K. Gosh, P. Mathivanan, J. Capiello, Tetrahedron: Asymmetry 9 (1998) 1.
[7] K.A. Jørgensen, M. Johannsen, S.L. Yao, H. Audrain, J. Thorhauge, Acc. Chem. Res. 32 (1999) 605.
[8] A. Pfaltz, Synlett (1999) 835.
[9] J.S. Johnson, D.A. Evans, Acc. Chem. Res. 32 (2000) 325.
[10] M.I. Burguete, J.M. Fraile, J.I. García, E. García-Verdugo, S.V. Luis, J.A. Mayoral, Org. Lett. 2 (2000) 3905.
[11] S. Orlandi, A. Mandoli, D. Pini, P. Salvadori, Angew. Chem. Int. Ed. Engl. 40 (2001) 2519.
[12] D. Rechavi, M. Lemaire, Org. Lett. 3 (2001) 2493.
[13] M.I. Burguete, J.M. Fraile, J.I. García, E. García-Verdugo, C.I. Herrerías, S.V. Luis, J.A. Mayoral, J. Org. Chem. 66 (2001) 8893.
[14] R.J. Clarke, I.J. Shannon, Chem. Commun. (2001) 1936.
[15] K. Hallman, C. Moberg, Tetrahedron: Asymmetry 12 (2001) 1475.
[16] J.K. Park, S.-W. Kim, T. Hyeon, B.M. Kim, Tetrahedron: Asymmetry 12 (2001) 2931.
[17] A. Corma, H. García, A. Moussaif, M.J. Sabater, R. Zniber, A. Redouane, Chem. Commun. (2002) 1058.
[18] M.I. Burguete, E. Díez-Barra, J.M. Fraile, J.I. García, E. García-Verdugo, R. González, C.I. Herrerías, S.V. Luis, J.A. Mayoral, Bioorg. Med. Chem. Lett. 12 (2002) 1821.
[19] J.M. Fraile, J.I. García, J.A. Mayoral, T. Tarnai, M.A. Harmer, J. Catal. 188 (1999) 214.
[20] P.J. Alonso, J.M. Fraile, J. García, J.I. García, J.I. Martínez, J.A. Mayoral, M.C. Sánchez, Langmuir 16 (2000) 5607.
[21] J.M. Fraile, J.I. García, C.I. Herrerías, J.A. Mayoral, M.A. Harmer, J. Mol. Catal. A 165 (2001) 211.
[22] C. Langham, S. Taylor, D. Bethell, P. McMorn, P.C. Bulman Page, D.J. Willock, C. Sly, F.E. Hancock, F. King, G.J. Hutchings, J. Chem. Soc., Perkin Trans. 2 (1999) 1043.
[23] S. Taylor, J. Gullick, P. McMorn, D. Bethell, P.C. Bulman Page, F.E. Hancock, F. King, G.J. Hutchings, J. Chem. Soc., Perkin Trans. 2 (2001) 1714.
[24] S. Taylor, J. Gullick, P. McMorn, D. Bethell, P.C. Bulman Page, F.E. Hancock, F. King, G.J. Hutchings, J. Chem. Soc., Perkin Trans. 2 (2001) 1724.
[25] D.A. Evans, K.A. Woerpel, M.M. Hinman, M.M. Faul, J. Am. Chem. Soc. 113 (1991) 726.
[26] J.M. Fraile, J.I. García, J.A. Mayoral, T. Tarnai, Tetrahedron: Asymmetry 8 (1997) 2089.
[27] J.M. Fraile, J.I. García, J.A. Mayoral, T. Tarnai, Tetrahedron: Asymmetry 9 (1998) 3997.
[28] A.I. Fernández, J.M. Fraile, J.I. García, C.I. Herrerías, J.A. Mayoral, L. Salvatella, Catal. Commun. 2 (2001) 165.
[29] J.M. Fraile, J.I. García, V. Martínez-Merino, J.A. Mayoral, L. Salvatella, J. Am. Chem. Soc. 123 (2001) 7616.
[30] G. Chelucci, M.G. Sanna, S. Gladiali, Tetrahedron 56 (2000) 2889.
[31] A.V. Bedekar, E.B. Koroleva, P.G. Anderson, J. Org. Chem. 62 (1997) 2518.
[32] K. Alexander, S. Cook, C.L. Gibson, Tetrahedron Lett. 41 (2000) 7135.