ELSEVIER

Journal of Molecular Catalysis A: Chemical 165 (2001) 211–218

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Bis(oxazoline)-metal complexes immobilised by electrostatic interactions as heterogeneous catalysts for enantioselective Diels–Alder reactions

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Received 9 June 2000; accepted 11 September 2000

Abstract

The immobilisation by cationic exchange of complexes of a bis(oxazoline) with Cu(II), Mg(II) and Zn(II) has been studied with two types of anionic solid, a laponite clay and a nafion-silica nanocomposite. The results obtained show that the cationic exchange depends on both the geometry of the complex and the nature of the cation. Whereas the immobilisation of square-planar complexes takes place easily, the situation is not the same for tetrahedral complexes. The solids prepared have been used as catalysts in a benchmark Diels–Alder reaction. These solids are efficient catalysts but the enantioselectivities are low, a fact that is related to the presence of non-chiral catalytic sites and to the nature of both the solid counter-ion and the bis(oxazoline) structure. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Bis(oxazoline); Diels–Alder; Catalyst

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1. Introduction

Enantioselective reactions promoted by chiral catalysts is a field of growing interest [1,2]. In particular, the development of effective chiral Lewis acid catalysts for Diels–Alder reactions has attracted considerable attention [3,4]. In this regard, the Diels–Alder reactions of prochiral dienes with 3-propenoyl and (*E*)-3-butenoyl-1,3-oxazolidin-2-ones have led to excellent results with catalysts related to binaphthol [5,6], as well as with zirconocene [7] and Ti-TADDOL catalysts [8–10]. The complexes of bis(oxazolines) [11–29] with several cations are effective catalysts in the aforementioned reactions and also in the hetero-Diels–Alder reaction of 1,3-cyclohexadiene with ethyl glyoxylate [29].

Within the field of chiral catalysis the development of heterogeneous catalysts that are able to promote enantioselective organic reactions is an area of particular interest [30–33]. With this aim in mind, we have explored the immobilisation of chiral Lewis acids [34] and, in particular, Ti-TADDOL derivatives [35,36] by formation of covalent bonds with organic polymers. However, the linking of the chiral auxiliary to the support through covalent bonds modifies the conformational preferences of the reactant-catalyst intermediates and, as a consequence, the asymmetric induction is altered. One possible way of avoiding this effect is the electrostatic immobilisation of cationic catalysts with anionic supports such as clays

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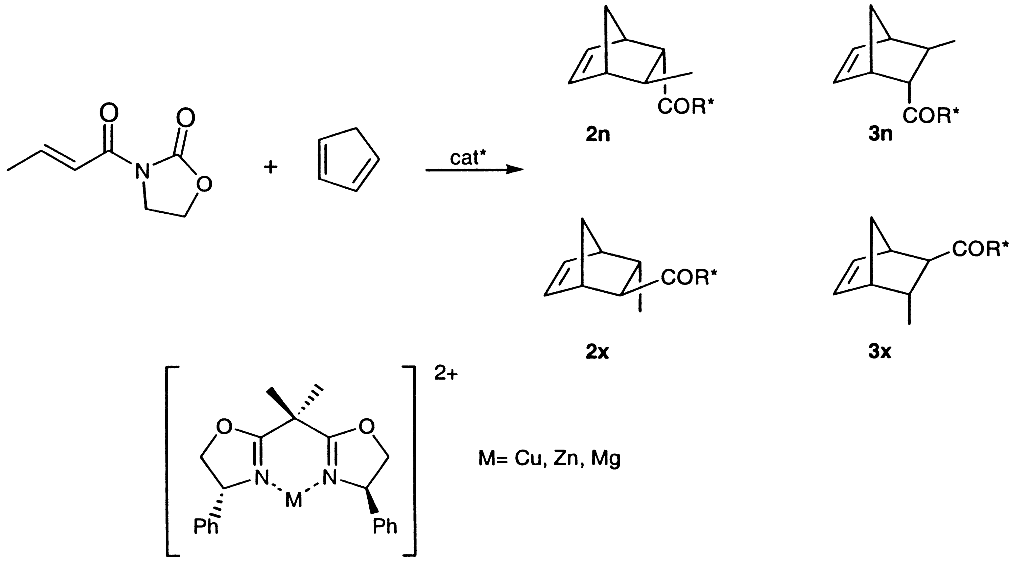
PII: S1381-1169(00)00423-4



Scheme 1.

[37,38] or anionic resins [39]. We have shown that cationic bis(oxazoline)-copper complexes can be immobilised by cationic exchange on clays [40–42] and on nafion or a nafion-silica nanocomposite [42,43]. The immobilised catalysts promote asymmetric cyclopropanation reactions and, in some cases, they can be recovered and reused without losing catalytic activity or selectivity. The same catalysts, when immobilised on zeolites, have been shown to promote enantioselective aziridination reactions [44].

In view of the above we considered it interesting to explore the use of bis(oxazoline)-cation complexes, immobilised by electrostatic interactions with anionic supports, as catalysts for the benchmark Diels–Alder reaction of (*E*)-3-butenoyl-1,3-oxazolidin-2-one with cyclopentadiene (Scheme 1).

2. Experimental

2,2′-Isopropylidene-[(4*R*)-4-phenyl-2-oxazoline] was obtained from (*R*)-phenylglycinol by following a previously described method [45]. Nafion-silica nanocomposite was obtained as previously described [42] and laponite was obtained from Laporte adsorbents.

2.1. Preparation of laponite-exchanged catalysts

Laponite (1 g) was slowly added to a solution of the bis(oxazoline) (1 mmol) and $M(OTf)_2$ (1 mmol) in methanol (20 ml) and the suspension was stirred for 24 h. The solid was filtered off, thoroughly washed with methanol and then dichloromethane, and dried before use.

2.2. Preparation of nafion-silica exchanged catalysts

Before exchange with the chiral complex, the solid was transformed into the sodium salt by passing through a NaCl solution until neutral pH was obtained. The solid was then washed with de-ionised water and dried under vacuum at 150°C for 4 h.

Nafion-silica (3 g) was added to a solution of the bis(oxazoline) (1 mmol) and $M(OTf)_2$ (1 mmol) in methanol (20 ml) and the suspension was stirred for 24 h. The solid was filtered off and thoroughly washed with methanol and then dichloromethane. The solid was dried under vacuum and ground in a mortar before use.

2.3. Characterisation of the catalysts

Metal analyses were carried out by plasma emission spectroscopy on a Perkin-Elmer 40 emission spectrometer. Nitrogen and carbon analyses were carried out on a Perkin-Elmer 2400 elemental analyser. Step-scanned X-ray diffraction (XRD) patterns of oriented samples were collected at room temperature from 3° in 2θ up to 60°, using a D-max Rigaku system with a rotating anode. The diffractometer was operated at 40 kV and 80 mA, the Cu $K\alpha$ radiation was selected using a graphite monochromator. Transmission FTIR of self-supported wafers evacuated ($<10^{-5}$ Torr) at different temperatures (50–200°C) were taken with a Mattson–Genesis series FTIR.

2.4. General procedure for the homogeneous Diels–Alder reaction

A solution of Cu(II), Zn(II) or Mg(II) triflate (0.4 mmol) and 2,2′-isopropylidene-[(4*R*)-4-phenyl-2-oxazoline] (0.44 mmol) in dry dichloromethane was stirred for 2 h under an argon atmosphere at room temperature. A solution of (*E*)-3-butenoyl-1,3-oxazolidin-2-one (155 mg, 1 mmol) was added by syringe and the solution was stirred at room temperature for 20 min. After this time, freshly distilled cyclopentadiene (792 mg, 12 mmol) was added by syringe and the solution was stirred at room temperature. The reaction was monitored by gas chromatography [FID, cross-linked methyl silicone column 30 m × 0.25 mm × 0.35 μm, helium as carrier gas at 20 psi, oven temperature program 190°C (1 min), 5°C min^{-1} to 200°C (10 min), retention times: 2.2 min (dienophile **1**), 4.6 min (cycloadducts **2** + **3**)]. After 22 h, a solution of $NaHCO_3$ was added and the mixture was vigorously stirred. The organic layer was separated and the aqueous phase extracted with dichloromethane. The combined organic phases were dried over anhydrous $MgSO_4$ and analysed by GC. The solvent was removed under reduced pressure and the conversion and endo/exo selectivity were determined by ^{1}H-NMR spectroscopy by integrating the signals corresponding to the methyl group (exo-cycloadducts **2*x*** + **3*x*** 0.83 ppm, endo-cycloadducts **2*n*** + **3*n*** 1.10 ppm, dienophile **1** 1.94 ppm). The endo cycloadducts were purified by column chromatography on silica gel, using *n*-hexane/EtOAc (2:1) as the eluent, and the enantiomeric excess was determined by ^{1}H-NMR spectroscopy in the presence of $Eu(hfc)_3$ (L/S molar ratio 0.3); in this way the absolute configuration of the major product was also determined [35].

2.5. General procedure for the heterogeneous Diels–Alder reaction

Before use the catalyst was dried under vacuum at 50°C for 24 h. To a suspension of the solid (100 mg of Laponite or 540 mg of nafion-silica) in dry dichloromethane, under argon, was added a solution of (*E*)-3-butenoyl-1,3-oxazolidin-2-one (46.5 mg, 0.3 mmol) by syringe and the suspension was stirred for 30 min. Freshly distilled cyclopentadiene (244 mg, 3.7 mmol) was added by syringe and the mixture stirred for the corresponding time (see Table 2). The reaction was monitored by GC. The catalyst was separated by filtration, thoroughly washed with dichloromethane and dried under vacuum before reuse. The solvent was evaporated under reduced pressure and the results determined as described above.

3. Results and discussion

In previous work [40] we studied the immobilisation of cationic bis(oxazoline)-copper complexes on several clays and the best results were obtained using Laponite as the anionic support. We, therefore, used this clay to support the complexes of 2,2′-isopropylidene-[(4*R*)-4-phenyl-2-oxazoline] with Cu(II), Zn(II), and Mg(II) triflates. Given that bis(oxazolines) are not very stable in aqueous media,

Table 1
Analyses of Laponite exchanged with the bis(oxazoline)-$M(OTf)_2$ complexes in methanol

Metal	M (mmol g^{-1})	N (mmol g^{-1})	C (mmol g^{-1})	d_{001} (Å)	Surface ($\text{m}^2\,\text{g}^{-1}$)
–	–	–	–	16.0	289
Cu	0.28	0.67	6.90	17.7	225
Zn	0.38	0.60	6.10	17.8	220
Mg	1.31	0.05	0.70	15.9	230

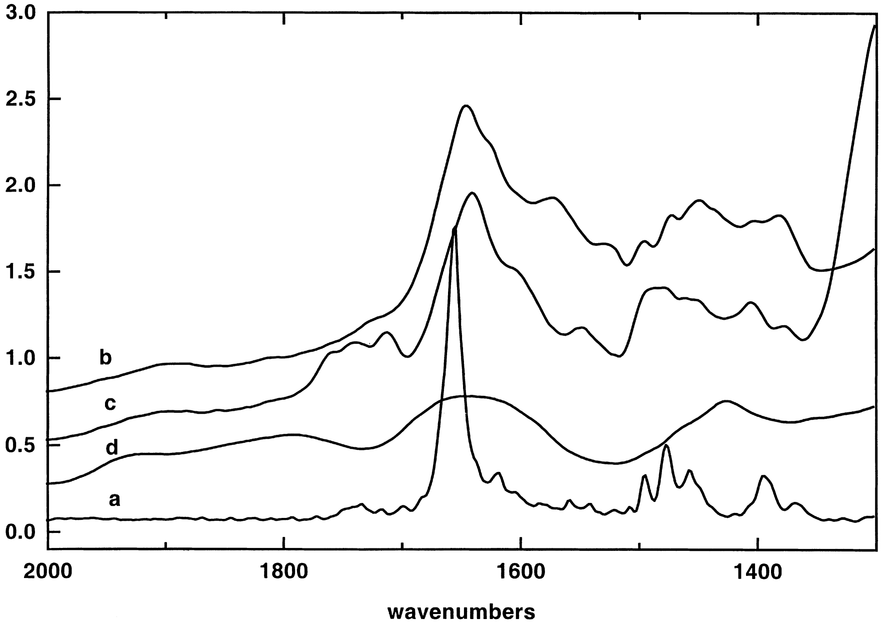


Fig. 1. IR spectra of the bis(oxazoline)-Cu(OTf)$_2$ (a) and of the laponites obtained from the cationic exchange with the complexes of the bis(oxazoline) with Cu(II) (b), Zn(II) (c) and Mg(II) (d).

cationic exchange was carried out in methanol. Table 1 shows the elemental, XRD and textural analysis data of the clays. The results obtained show three different kinds of behaviour depending on the metal. The complex bis(oxazoline)-Cu(II) gives rise to a clay with expanded basal spacing and reduced surface area, a situation in agreement with the exchange of a large complex that is, at least in part, accommodated within the interlamellar space of the clay, and the N/Cu ratio is near the theoretical value for the complex. The exchange of the bis(oxazoline)-Zn(II) complex also gave rise to a clay with expanded basal spacing and reduced surface area, although in this case the N/Zn ratio is lower than the theoretical value. Although this result must be considered with caution given the experimental error of the analyses, it indicates that some of the exchanged Zn(II) (about 20%) is not complexed by the bis(oxazoline). The carbon analysis confirms this hypothesis in that the C/N ratio is in good agreement with the theoretical value for the chiral ligand. Finally, the clay obtained from the bis(oxazoline)-Mg(II) complex does not show expanded basal spacing and it contains an unexpectedly high amount of Mg. These results, together with those obtained from the N and C analyses, indicate that the amount of complex exchanged, if any, is very low and that most of the Mg exchanged is free of chiral ligand.

Confirmation of these results was obtained from the FTIR spectra of the different clays. The homogeneous complexes show a C=N band at 1660–1670 cm^{-1} and a series of bands in the region 1450–1520 cm^{-1}. These bands are also identified in the Laponites exchanged with the Cu(II) and Zn(II) complexes, but not in the spectrum of the clay prepared from the Mg(II) complex (Fig. 1).

The clays were tested as catalysts in the benchmark Diels–Alder reaction of (*E*)-3-butenoyl-1,3-oxazolidin-2-one with cyclopentadiene (Scheme 1). The results obtained, along with those of the corresponding homogeneous reactions, are gathered in Table 2. All the solids promote the reaction and are more active than the original Laponite. In the homogeneous phase the Mg(II) catalyst is the most enantioselective, whereas the reaction with the Mg-based heterogeneous catalyst is not enantioselective at all. This lack of enantioselectivity is in agreement with the fact that the cation exchanged is not complexed by the chiral ligand. The reactions promoted by the clays exchanged with the

Table 2
Results obtained from the Diels–Alder reactions catalysed by the immobilised catalyst

Metal	Support	Time (h)	% conv.[a]	endo/exo[a]	% ee[b]
–	Laponite	40	13	75:25	–
–	Silica gel	40	57	85:15	–
Cu	–	22	99	88:12	19
Zn	–	22	97	90:10	29
Mg	–	22	95	76:24	69
Cu	Laponite	22	74	75:25	11
Cu	Laponite[c]	22	73	78:22	9
Zn	Laponite	22	67	77:23	7
Zn	Laponite[c]	22	70	75:25	0
Mg	Laponite	22	100	83:17	0
Cu	Nafion-silica	22	93	83:17	8
Zn	Nafion-silica	69	61	82:18	0
Mg	Nafion-silica	22	85	90:10	0

[a] Determined by ^{1}H-NMR spectroscopy.

[b] Determined in the endo cycloadducts by ^{1}H-NMR spectroscopy in the presence of Eu(hfc)$_3$, ***2n*** is the major product.

[c] Recovered catalyst.

Cu(II) and Zn(II) complexes are less enantioselective than the corresponding homogeneous processes. In the case of Cu(II), the heterogeneous catalyst is only slightly less enantioselective than the homogeneous one and it can be reused with the same enantioselectivity. On the other hand, the reduction in the enantioselectivity is more significant in the case of the Zn(II) heterogeneous catalyst and, furthermore, it leads to a racemic mixture upon recovery. The analyses of the recovered Cu(II) clay do not show leaching of copper but the carbon and nitrogen contents are noticeably increased (molar N/Cu ratio = 4.2), indicating that some reagent and/or product remains adsorbed on the clay. The appearance of a strong C=O band at 1736 cm^{-1} in the FTIR spectrum (Fig. 2) agrees with this hypothesis. In the case of the Zn(II) clay the recovered catalyst shows the same Zn and N contents and, as a consequence, the same N/Zn molar ratio. However, the FTIR spectrum (Fig. 2) presents a strong C=O band at 1736 cm^{-1}, which seems to indicate that the bis(oxazoline) is, at least in part, substituted by the dienophile and/or product in the co-ordination sphere of the cation, a situation in agreement with the loss of enantioselectivity in the reaction promoted by the recovered catalyst.

It has been described [21–27] that the nature of the counter-ion noticeably influences the Lewis acidity and the behaviour of the catalyst. We, therefore, studied the effect of the solid counter-ion by comparing the Laponite and a nafion-silica

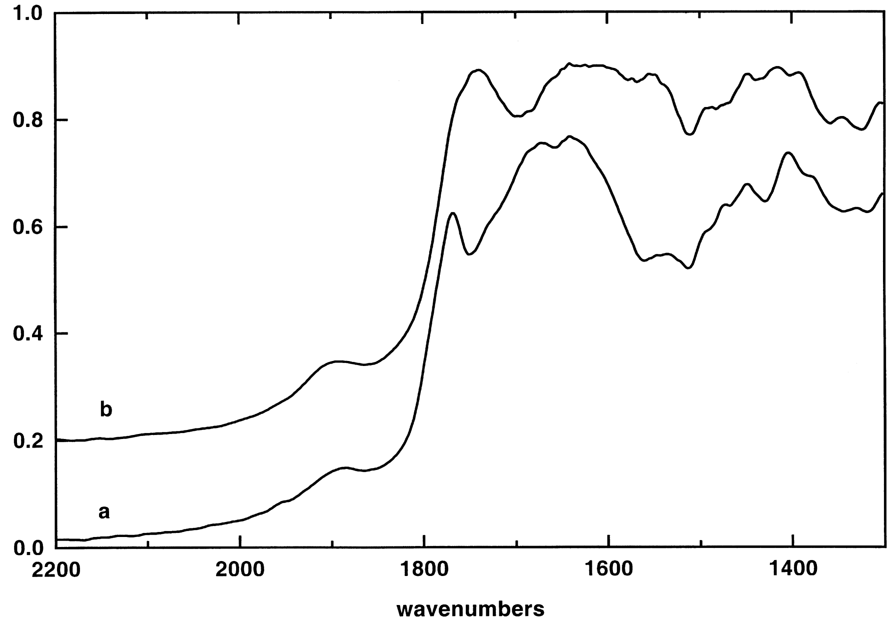


Fig. 2. IR spectra of the Laponites exchanged with the bis(oxazoline)-Cu(II) (a) and -Zn(II) (b) complexes after recovery.

Table 3
Analyses of nafion-silica exchanged with the bis(oxazoline)-M(OTf)$_2$ complexes in methanol

Metal	As prepared (mmol g^{-1})	Recovered (mmol g^{-1})	Surface (m^2 g^{-1})
Cu	0.05	0.05	84
Zn	0.06	0.05	80
Mg	0.09	0.08	77

nanocomposite. This change of support has a positive effect on the bis(oxazoline)-copper-catalysed cyclopropanation [42]. The cationic exchange was carried out from the sodium form of the nafion-silica nanocomposite with a methanolic solution of the the complexes of 2,2′-isopropylidene-[(4*R*)-4-phenyl-2-oxazoline] with Cu(II), Zn(II), and Mg(II) triflates. The results obtained from the analyses of the solids are shown in Table 3. The small amount of exchanged complexes makes the nitrogen analyses unreliable, so the presence of bis(oxazoline) was studied by examination of the FTIR spectra (Fig. 3). Whereas the solids obtained from the Cu(II) and Zn(II) complexes show the bands corresponding to the chiral ligand, the solid obtained from the Mg(II) complex does not show such bands. The nitrogen analysis of the solution obtained from the cationic exchange of this complex shows that most of the bis(oxazoline) remains in solution, meaning that most of the immobilised Mg(II) is again free of chiral ligand.

The three nafion-silica catalysts were tested in the same Diels–Alder reaction (Scheme 1). The results obtained (Table 2) show that the solids containing Cu(II) and Mg(II) are more active than the Zn(II) catalyst, which has an activity similar to that of pure silica gel. With regard to the asymmetric induction, the immobilised Cu(II) complex is the only one leading to an enantiomeric excess. The lack of enantioselectivity in the reaction promoted by the magnesium

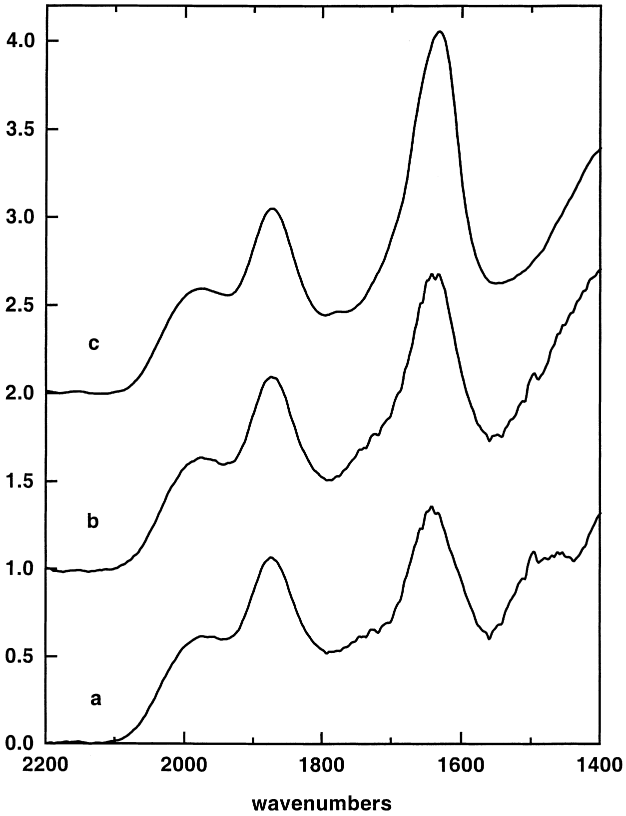


Fig. 3. IR spectra of the nafion-silica exchanged with the bis(oxazoline)-Cu(II) (a), -Zn(II) (b) and -Mg(II) (c) complexes.

solid is in agreement with the absence of chiral catalytic centres in the solid, whereas the behaviour of the Zn(II)-immobilised system may be related to the catalytic role of the support as a non-enantioselective catalyst.

It has been shown [41] that bis(oxazoline)-Cu(II) complexes immobilised on Laponite retain the square-planar geometry, with the surface of the clay sheets acting as the negative counter-ions. The results obtained in this work demonstrate that the exchange of tetrahedral bis(oxazoline)-M(II) complexes is not so efficient. In the case of Mg(II) the complex is not exchanged, whereas in the case of the Zn(II) complex the cationic exchange leads to a solid containing both complexed and non-complexed Zn(II). Furthermore, the bis(oxazoline) can be easily replaced in the Zn(II) complex by the dienophile and/or product, both of which act as ligands. The use of a support with a lower co-ordinating ability, such as the nafion-silica nanocomposite, does not change the situation described above. It is not easy to give an explanation for the differences between the immobilisation of square-planar and tetrahedral complexes. It is probable that the immobilised tetrahedral complexes are less stable due to the existence of stronger steric interactions between the chiral ligand and the support. In this respect, the size of the cation would modify these steric interactions, which may account for the differences between Zn(II) and Mg(II).

The results obtained show that the bis(oxazoline)-cation complexes immobilised by electrostatic interactions with anionic supports are not suitable as catalysts for enantioselective Diels–Alder reactions for several reasons. On the one hand, the cationic exchange strongly depends on the geometry of the complex to be immobilised. Whereas square-planar copper complexes are easily exchanged, the situation is not the same with tetrahedral complexes. In these cases some of the cation exchanged is not complexed by the chiral ligand, giving rise to the formation of non-chiral catalytic sites. Furthermore, the strong co-ordinating ability of the dienophile and products is an additional problem because they can replace the bis(oxazoline) in the co-ordination sphere of the cation. In the homogeneous phase the 2,2′-isopropylidene-[(4*R*)-4-phenyl-2-oxazoline] leads to high enantioselectivities when it is incorporated in tetrahedral complexes. With square-planar complexes the best enantioselectivities are obtained using the 2,2′-isopropylidene-[(4*S*)-4-*tert*-butyl-2-oxazoline] [22]. In view of this, the immobilisation of the 2,2′-isopropylidene-[(4*S*)-4-*tert*-butyl-2-oxazoline]-Cu(II) complex may be envisaged as being advantageous. However, it has been shown [42] that the immobilisation of this complex is hampered by the strong steric interactions between the bulky chiral ligand and the support. In summary, it can be concluded that the steric interactions between the complex to be immobilised and the support impose severe limitations on the utility of the catalysts heterogeneised in this way.

On the other hand, the co-ordinating ability of the solid counter-ion cannot be reduced to the same extent as in solution. The less-coordinating solid counter-ions are those related to nafion, which are similar to triflate. Evans has suggested [21] that triflate does not completely dissociate in bis(oxazoline)-copper complexes, leading to the formation of intermediate species in which the dienophile and the catalyst do not form a chelate complex but a less organised catalyst-dienophile intermediate.

4. Conclusions

The steric interactions between the chiral auxiliary and the support impose certain limitations on the immobilisation of bis(oxazoline)-cation complexes by electrostatic interactions with an anionic support. These steric interactions depend on both the geometry of the complex and the size of the chiral auxiliary. These difficulties are clearly shown in the use of these solids as catalysts in asymmetric Diels–Alder reactions, in which the co-ordinating ability of reagents and products also plays a crucial role. Finally, the use of solid counter-ions of low co-ordinating ability is strongly recommended. However, it is not possible to reduce this co-ordinating level to below that of fluorosulfonic acids.

Acknowledgements

This work was made possible by the generous financial support of the Comisión Interministerial de Ciencia y Tecnología (Project MAT99-1176).

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