

Cyclopropanation reactions catalysed by copper and rhodium complexes homogeneous and heterogenised on a modified USY-zeolite. Influence of the catalyst on the catalytic profile

M.J. Alcón ^a, A. Corma ^b, M. Iglesias ^{c,*}, F. Sánchez ^{a,1}

^a Instituto de Química Orgánica, CSIC, Juan de la Cierva, 3, 28006 Madrid, Spain

^b Instituto de Tecnología Química, UPV-CSIC, Avda. de los Naranjos s/n, 46022, Valencia, Spain

^c Instituto de Ciencia de Materiales de Madrid, CSIC, Serrano 113 bis, Cantoblanco, 28049 Madrid, Spain

Received 25 June 1998; accepted 13 October 1998

Abstract

The reaction of alkyl diazoacetate (ethyl and *t*-butyl diazoacetate) with styrene and 1,2-dihydropyrene is catalysed by Cu- and Rh-complexes, homogeneous and heterogenised on a modified USY-zeolite. A comparative study (homogeneous vs. supported) was made for the catalytic activity and selectivity in cyclopropanation reactions. High activities and selectivity (cyclopropanation vs. dimerisation) were obtained at 1:150 catalyst:substrate relationship, with the Cu catalysts being remarkably more active than the Rh-ones. The enantioselectivity in the tested conditions was low. The reactivity and selectivity for zeolite-heterogenised catalysts do not deviate significantly from that obtained using the corresponding homogeneous complexes, though they could be used without loss of cyclopropanation activity and metal leaching at least in five successive runs. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Cyclopropanation; Copper; Rhodium; Heterogenised catalyst; Zeolite

1. Introduction

The development of new methods for the efficient and selective preparation of cyclopropanes is of great interest in organic chemistry due to the frequent existence of these structures in biologically active compounds [1,2] and their role as valuable synthetic intermediates [3–7]. The direct transfer of carbene from

diazo compounds to alkenes, which is the most straightforward route to cyclopropanes, is catalysed by transition metals and the use of several metal complexes has been described [8–14]. Catalysts based in chiral transition metal complexes permit the control of the enantioselectivity in cyclopropanations [15–20].

During the last few years a great deal of effort has been devoted to the development of heterogeneous systems able to promote organic reactions [21]. Although organic supports have been used frequently, the advantages of inorganic ones with respect to stability have been

* Corresponding author. Tel.: +34-91-3349032; Fax: +34-91-3720623; E-mail: immih3n@fresno.csic.es

¹ Also corresponding author.

pointed out in the literature [22,23]. Nevertheless, it is generally reported that when anchoring organometallic complexes on both organic [24] and inorganic [25] supports their intrinsic catalytic activity is reduced. Since the rate of a given reaction depends on both the intrinsic rate constant and reactant concentration, it becomes apparent that the decrease in the intrinsic activity of a homogeneous catalyst when anchored could be compensated for by increasing the concentration of reactants in their proximity due to an interaction with strong electric charges present on the surface. This effect could be

achieved through an appropriate choice of support, which can act positively by absorbing the reactant molecules and increasing their concentration in the proximity of the organometallic active sites. Zeolite complexes might offer advantages as catalysts because of the high dispersion of the metal ions and because the zeolite pore structure possibly influences the selectivity of the reaction. The zeolite lattice might act as a large rigid ligand to the metal ions, thereby influencing the stereochemical outcome of the reaction of an olefin with alkyl diazoacetates. The formation of polymeric side-products, fre-

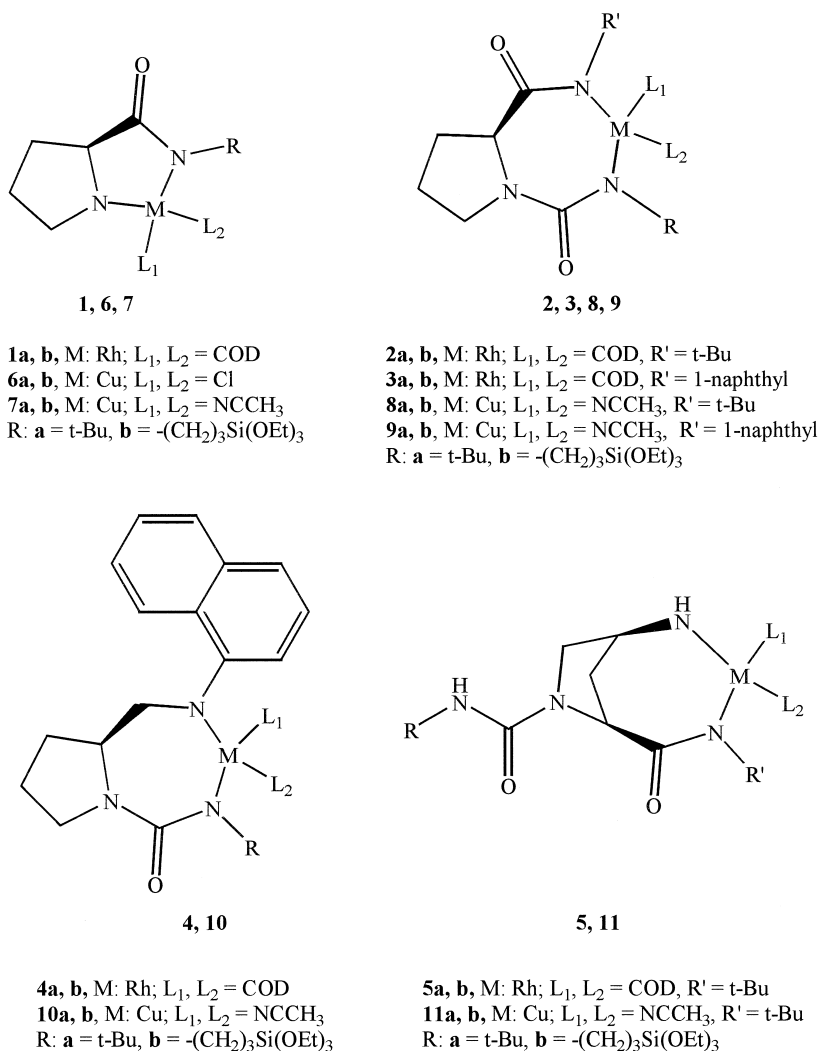


Fig. 1.

quently observed in Cu(I) systems, was expected to occur with greater difficulty inside the zeolite mesopores, increasing the catalyst stability in the reaction media.

In previous papers, we have described the synthesis and characterisation of a series of chiral Rh and Cu complexes and the corresponding heterogenised complexes on zeolite catalysts [26,27] and their preliminary results in catalysed hydrogenation and cyclopropanation [28]. This paper presents data on the use of a series of Rh(I) and Cu(I) complexes and the respective heterogenised zeolite complexes (Zeol–Rh(I) and Zeol–Cu(I)) (Fig. 1) in catalysed α -diazoester cyclopropanation of styrene and 1,2-dihydropyrene. We have studied the effect of the ligands and the role of support on the catalytic profile of these complexes.

2. Experimental

2.1. General methods and chemicals

All preparations of Rh and Cu complexes were carried out under dinitrogen by standard Schlenk techniques. All solvents were carefully degassed before use. The silylating agent $\text{OCN}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$ was obtained from Fluka (96%) and was distilled before use. C, H and N analyses were carried out by the Analytical Department of the Institute of Organic Chemistry and the Institute of Materials Science (CSIC) with a Heraeus and a Perkin-Elmer 240C apparatus, respectively. Metal contents were analysed by atomic absorption using a Unicam (SP9) Philips apparatus. The conductometric experiments were carried out in acetonitrile solutions (ca. 10^{-3} M) with a Philips Pw5906 conductometer equipped with a Philips PW 9510/60 conductometric cell. IR spectra were recorded with a Nicolet XR60 spectrophotometer (range 4000–200 cm^{-1}) in KBr pellets; ^1H and ^{13}C NMR spectra were taken on Varian XR300 and Bruker 200 spectrometers; ^1H NMR chemical shifts are given in ppm using tetram-

ethylsilane as an internal standard. Optical rotation values were measured at the sodium-D line (589 nm) with a Perkin Elmer 241 MC polarimeter. Gas chromatography was performed using a Hewlett-Packard 5890 II with a flame ionisation detector in a cross-linked methylsilicone column.

The inorganic support taken as model is a USY-zeolite prepared by steam calcination at 1023 K of an 80% ammonium-exchanged NaY (SK40 Union Carbide), followed by treatment with a 1 N citric acid solution at 333 K for 30 min to remove extra-framework species. After this, the zeolite was thoroughly washed and dried at 403 K for 6 h. The final zeolite had a well-developed mesopore system (pore diameter 12–30 Å besides the typical ~ 12 Å micropores). The controlled dealumination promotes destruction of some sodalite units, which allowed direct communication between α -cages generating cavities wider than 12 Å. The formation of supermicropores and large mesopores has been detected by N_2 adsorption–desorption. The main characteristics of the resultant zeolite are: unit cell size, 24.40 Å; bulk $\text{SiO}_2/\text{Al}_2\text{O}_3$, 4.2; crystallinity, greater than 95%. The inorganic support was dried at 415 K under 0.01 Torr before the anchoring process.

2.2. Synthesis of Rh-complexes

The Rh(I) complexes (**1–5a,b**) were synthesised according to previously published methods [28,29], which could be exemplified in the following.

To a solution of di- μ -chloro-bis(1,5-cyclooctadiene)dirhodium (0.4 mmol) in dry dichloromethane (20 ml) was successively added a solution of the ligand (0.8 mmol) in dichloromethane (2 ml) and ammonium hexafluorophosphate (0.8 mmol). The mixture was stirred for 3 h at room temperature under argon atmosphere and filtered. The filtrate was evaporated under reduced pressure to 2 ml. Careful addition of diethyl ether caused the precipitation of a yellow-orange solid which was collected by fil-

tration, washed with ethyl ether and dried in vacuum to give the desired cationic complex.

2.2.1. $[Rh(COD)\{(2S,4S)\text{-}1,2\text{-}(bis\text{-}t\text{-butylaminocarbonyl}\text{-}4\text{-aminopyrrolidine})\}PF_6]$ (**5a**)

Yield: 76%. Yellow powder, m.p.: 215°C (dec.). $[\alpha]_D^{25} = -28$ (MeOH, 0.5). $\Lambda(CH_3CN)$ ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) = 129. Anal. Found: C, 39.1; H, 5.9; N, 8.8; Rh, 16.0. $C_{22}H_{40}F_6N_4O_2PRh$. Calc.: C, 41.3; H, 6, 3; N, 8.8; Rh, 16.1%. IR (cm^{-1}): $\nu(NH)$ 3380, 3310, 3180; $\nu(C=O)$ 1640, 1600. 1H NMR (CD_3CN): $\delta = 8.01$ (br, 1H, NH); 6.30 (br, 1H, NH); 4.8–4.6 (d, 1H, $CH\text{-CONH-}$); 4.51 (m, 1H, $CH\text{-NH}_2$); 4.22 (d, 2H, NH_2); 3.40 (m, 2H, $CH_2\text{-NCO}$); 1.9–1.3 (m, 2H, $CH_2\text{-CHCONH}$); 1.3–1.2 (18H, $\text{-C(CH}_3)_3$).

2.2.2. $[Rh(COD)\{(2S,4S)\text{-}1\text{-}(3\text{-triethoxysilylpropyl)aminocarbonyl}\text{-}2\text{-}t\text{-butylaminocarbonyl}\text{-}4\text{-aminopyrrolidine})\}PF_6]$ (**5b**)

Yield: 71%. Green-yellow powder, m.p.: 235°C (dec.). $[\alpha]_D^{25} = -18.3$ (MeOH, 0.6). Anal. Found: C, 40.5; H, 6.8; N, 7.2; Rh, 13.0. $C_{27}H_{52}F_6N_4O_5PRhSi$. Calc.: C, 40.2; H, 6.8; N, 7.2; Rh, 13.1%. $\Lambda(CH_3CN)$ ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) = 108. IR (cm^{-1}): $\nu(NH)$ 3300; $\nu(C=O)$ 1650; $\nu(Si\text{-O})$ 1100. 1H NMR ($CDCl_3$): $\delta = 7.90$ (br, 1H, $CONH\text{-}$), 4.71 (m, 1H, $CH\text{-CONH}\text{-C(CH}_3)_3$), 4.5–4.4 (m, 1H, $CH\text{-NH}_2$), 3.9–3.7 (q, 6H, $O\text{-CH}_2\text{-CH}_3$), 3.4–3.2 (m, 2H, $CH_2\text{-N}$); 3.2–3.0 (m, 2H, $NCON\text{-CH}_2\text{-}$), 2.4–2.2 (m, 2H, $CH_2\text{-CHCONH}$), 1.7–1.6 (m, 2H, $Si\text{-CH}_2\text{-CH}_2\text{-CH}_2$); 1.33 (s, 9H, $C(CH_3)_3$); 1.15 (t, 9H, $OCH_2\text{-CH}_3$); 0.65 (t, 2H, $CH_2\text{-Si}$).

2.3. Synthesis of the Cu(I) complexes

The copper complexes (**6–11a,b**) were obtained as described in the literature [26,27]. To a

Table 1

Dependence of the chemical yield, selectivity and optical yield on the reaction temperature

Catalyst	T (°C)	Selectivity ^a (% yield)	Cis/trans	(% ee)	
				cis	trans
1a	25	78 (50)	0.86	6	8
	50	93 (82)	0.69	3	4
	80	95 (99)	0.70	2	3
Zeol-1b	25	90 (20)	0.75	–	–
	50	96 (51)	0.59	–	–
	80	100 (72)	0.53	–	–
6a	–20	38 (40)	0.50	20	29
	0	74 (46)	0.55	18	24
	25	96 (99)	0.58	16	23
	80	92 (99)	0.55	10	17
Zeol-6b	–20	35 (40)	0.70	–	–
	0	63 (46)	0.82	3	5
	25	100 (77)	0.86	1	2

Styrene:diazoacetate = 8 mmol:11 mmol; without solvent, styrene:catalyst = 150/1.

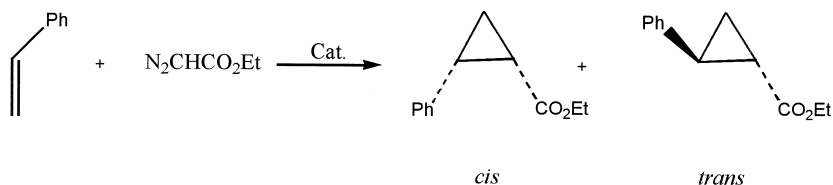
^aReaction products vs. ethylfumarate and ethyl maleate.

solution of $[Cu(CH_3CN)_4]ClO_4$ (0.4 mmol) in dry acetonitrile (20 ml) was added a solution of the ligand (0.4 mmol); the mixture was stirred for 3 h at room temperature and filtered. The filtrate was evaporated under reduced pressure to a volume of 5 ml. The careful addition of diethyl ether caused the precipitation of a microcrystalline solid, which was collected by filtration, washed and dried in vacuum to give the desired complex.

2.4. Heterogenisation of Rh(I) and Cu(I) complexes on USY-zeolites

The supported Rh and Cu(I) complexes (**Zeol-1b–Zeol-5b**; **Zeol-6b–Zeol-11b**) were prepared as we have previously described [27,28].

The heterogenisation of $[Rh(COD)\{(2S,4S)\text{-}1\text{-}(3\text{-triethoxysilylpropyl})\text{-}2\text{-}t\text{-butylamino}$ car-



Scheme 1.

Table 2
Effect of the concentration in the cyclopropanation reaction of styrene

Catalyst	Solvent	Selectivity (% yield)	<i>cis</i> / <i>trans</i>	(% ee)	
				<i>cis</i>	<i>trans</i>
1a	not	78 (50)	0.69	6	8
	ClCH ₂ -CH ₂ Cl	70 (30)	0.71	2	3
Zeol-1b	not	60 (5)	0.58	2	2
	ClCH ₂ -CH ₂ Cl	53 (5)	0.66	2	2
6a	not	96 (99)	0.58	16	23
	CH ₂ Cl ₂	86 (78)	0.53	10	13
Zeol-6b	not	100 (77)	0.82	1	2
	CH ₂ Cl ₂	73 (91)	0.88	< 5	< 5
7a	not	88 (83)	0.66	1	2
	CH ₃ CN	82 (28)	0.44	0	0
Zeol-7b	not	63 (87)	0.52	< 5	< 5
	CH ₃ CN	69 (66)	0.60	0	0

Temperature 25°C, styrene/diazoacetate = 8/11.

bonyl-4-aminopyrrolidine}PF₆ (**5b**) was performed as follows. A solution of **5b** (0.2 mmol) in dry dichloromethane (2 ml) was added to a well-stirred suspension of the inorganic support (modified USY-zeolite dried at 140°C/0.1 mm Hg for 3–4 h) (1 g). The mixture was stirred at room temperature for 24 h. The solid was then filtered and Soxhlet-extracted with dichloromethane–ethyl ether (1:2) for 7–24 h to remove the remaining non-supported complex. The pale-yellow solid was dried in vacuum.

2.5. Cyclopropanation reactions

2.5.1. General procedure

To a stirred mixture of olefin (8 mmol) and catalyst (0.02 mmol), alkyl diazoacetate (11 mmol) was added dropwise with a syringe pump over a period of 2 h in inert atmosphere at labile

temperature. After the evolution of N₂ ceased, the product mixture was fractionated under reduced pressure. The chemical and the optical yields are determined by gas chromatography using a chiral glass capillary column (mixture of methylsilicone (OV-1701) and permethylcyclodextrine (90:10)).

3. Results and discussion

3.1. Synthesis and characterisation of metal complexes

The complexes were prepared by addition of a stoichiometric amount of donor to a solution of complex precursor ([RhCl(COD)]₂, [Cu(CH₃CN)₄]ClO₄) as described in Section 2. The cationic complexes were isolated as yellow or pale-green air-stable solids. The structure of the metal complexes was well established by analytical and spectroscopic analysis.

Preparations of zeolite heterogenised complexes were carried out for complexes **1b–11b**, bearing a –CH₂CH₂CH₂Si(OEt)₃ group, by controlled hydrolysis of Si–OEt bonds and reaction with the free silanol (Si–OH) on the surface of a USY-zeolite. The resulting catalytic material is very stable and the species are covalently bonded to the surface. The fact that the structures of the starting complexes are maintained when attached to the surface was confirmed by spectroscopic data. It is unlikely that the nature of the complex is substantially altered under the relatively mild conditions of the anchoring reaction [30]. The loading of metal is

Table 3
Dependence of the chemical yield, selectivity and enantioselectivity on the ratio styrene:diazoacetate

Catalyst	Styrene/diazoacetate (mmol/mmol)	Selectivity (% yield)	Diastereoselectivity (<i>cis</i> / <i>trans</i>)	% ee	
				<i>cis</i>	<i>trans</i>
6a	8:11	86 (78)	0.53	10	13
	8:16	67 (75)	0.54	10	14
Zeol-6b	8:11	73 (91)	0.88	< 5	< 5
	8:16	58 (51)	1.12	1	1

Solvent: 2 ml CH₂Cl₂, temperature: 25°C.

always ca. $\sim 1\text{--}2\%$ ($\pm 0.1\%$) measured by atomic absorption of metal (Rh or Cu) of the digested samples. These values have been used for calculating the ratio catalyst/substrate in the reaction tests. These heterogenised complexes are characterised by IR and UV–vis spectroscopy and elemental analysis of C, H, N and Rh.

3.2. Catalytic cyclopropanation

Cyclopropanation of styrene and 1,2-dihydropyrene by alkyl diazoacetates (alkyl = ethyl, *t*-butyl) was carried out making use of the zeolite–metal complexes upon decomposition of alkyl diazoacetate. The results were compared with those obtained with homogeneous metal complexes. We have studied the influence of the different parameters on the reaction, especially the role of the support on the intrinsic activity of the heterogenised catalysts, as well as the surface concentration effect and the geometrical constrains.

3.2.1. Cyclopropanation of styrene

In the reaction of styrene with ethyl diazoacetate the main product is ethyl *cis/trans*-2-phenylcyclopropanecarboxylate. In this reaction two new asymmetric centres are generated, which causes a total of four stereoisomers (Scheme 1). Also, diethyl maleate and diethyl fumarate are formed as by-products.

In the standard cyclopropanation reaction, ethyl diazoacetate is added to styrene in 2 h using a syringe pump. The reactions are carried out in the absence of a solvent. The complexes are dissolved or suspended in styrene prior to the addition of ethyl diazoacetate. After dissolu-

tion of the catalyst, the dropwise addition of ethyl diazoacetate is started, the beginning of the reaction is indicated by a spontaneous evolution of N_2 .

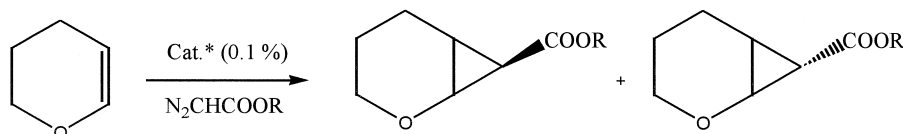
In the following tables, the ranges of the chemical yield and optical yields are given for ethyl *cis/trans*-2-phenylcyclopropanecarboxylate, found with varying parameters such as reaction temperature, ratio of styrene to ethyl diazoacetate, catalyst type, and concentration of reactants.

In the system styrene/ethyl diazoacetate, the influence of the reaction temperature on the chemical and optical yields and selectivity for two related homogeneous and heterogenised Rh and Cu catalysts, is summarised in Table 1. All catalysts showed high catalytic activity and selectivity (cyclopropanation vs. dimerisation) that increases when the temperature increases, while the diastereoselectivity (*cis/trans* relationship) and the optical yields of obtained cyclopropanes decreased with temperature increase.

The results from the cyclopropanation reactions carried out at different concentration using adequate solvent or no solvent are shown in Table 2. In all cases, the use of solvent decreases yield and selectivity, although care must be taken to avoid excess diazoacetate at any moment during the reactions, that increases the formation of diethyl maleate and fumarate.

The results of the variation of the ratio styrene–ethyl diazoacetate are shown in Table 3 and indicates that a ratio of 8:11 is more convenient for chemical yield and selectivity. Similar results were published by Brunner et al. for other types of Rh and Cu catalysts [31,32].

Table 4a,b shows the results obtained by variation of the diazoacetate. The *cis/trans* se-



Scheme 2.

lectivity increases with increasing volume of diazoacetate. The chemical yields for Rh catalysts are similar; for Cu derivatives they decrease. The optical yield does not change significantly and is higher for the *trans* product than for the *cis* product.

After these parameter dependence studies, we have established that the decomposition of diazoacetates and subsequent cyclopropanation reactions, independently for substrate and diazoacetate would be tested at room temperature (25°C) for Cu-catalysts and 50°C for less active Rh complexes. The styrene:diazoacetate ratio could be 8:11, and addition of the diazoacetate should be slow, in order to avoid an excess of reagents in the reaction media. In these conditions the reaction rates were easily obtained and for synthetical purposes the total conversion was obtained in a few hours.

3.2.2. Cyclopropanation of 1,2-dihydropyrene

In the reaction of 1,2-dihydropyrene with ethyl diazoacetate the main product is ethyl *cis/trans*-2-cyclopropanecarboxylate, and as a normal side reaction, dimerisation of alkyl diazoacetate fragments leading to ethyl maleate and ethyl fumarate is observed. (Scheme 2). The results for the reaction of 1,2-dihydropyrene with ethyl diazoacetate are given in Tables 5–7.

In an attempt to improve the enantio- and diastereoselectivities of the reaction, we exam-

Table 5

Dependence of the chemical yield, selectivity and optical yield on the reaction temperature

Catalyst	T (°C)	Selectivity ^a (% yield)	Cis / trans	% ee	
				cis	trans
1a	25	51(47)	0.26	2	7
	50	63(83)	0.30	< 5	< 5
Zeol-1b	25	60(10)	0.16	0	0
	50	67(35)	0.18	0	0
7a	25	61(95)	0.16	1	7
	60	77(91)	0.15	3	11
Zeol-7b	25	45(73)	0.14	< 5	< 5
	60	71(98)	0.17	4	13

1,2-Dihydropyrene:diazoacetate = 8 mmol:11 mmol; without solvent, substrate:catalyst = 150/1.

^aReaction products vs. ethylfumarate and maleate.

Table 6

Effect of the concentration in the cyclopropanation reaction of 1,2-dihydropyrene

Catalyst	Solvent	Selectivity (% yield)	Cis / trans	% ee	
				cis	trans
7a	not	83(87)	0.11	2	3
	CH ₃ CN	57(86)	0.15	1	7
Zeol-7b	not	68(72)	0.11	1	3
	CH ₃ CN	45(71)	0.14	3	5

Temperature 25°C, substrate/diazoacetate = 8/11.

ined the effect of temperature (Table 5). All catalysts show high catalytic activity and selectivity that increases when the temperature increases; diastereoselectivity and enantioselectivity also are increased slightly with the temperature. The use of solvent diminishes the chemical yield and selectivity and increases the formation of diethyl maleate and fumarate (Table 6). The effect of ligand structure on chemical yield and selectivity is shown in Table 7. As can be seen the data for the five-member chelates are similar to that of the seven-membered.

It is worth noting that deactivation of the catalyst does not occur since the addition of more reactant is possible, although the use of a large amount of catalyst does not improve the yield of the reaction. The asymmetric induction for unsupported and zeolite-heterogenised complexes is found to be similar.

Table 7

Chemical yield and selectivity for Cu-complexes (t = 25°C, without solvent)

Catalyst	Selectivity (% yield)	Cis / trans	% ee	
			cis	trans
6a	83(99)	0.17	1	7
Zeol-6b	78(68)	0.10	3	5
7a	84(97)	0.11	2	4
Zeol-7b	68(72)	0.14	3	5
8a	88(95)	0.22	2	4
Zeol-8b	87(86)	0.07	1	5
9a	89(98)	0.10	1	2
Zeol-9b	97(81)	0.08	3	5
10a	88(98)	0.18	1	7
Zeol-10b	66(62)	0.11	2	18

4. Conclusions

We have shown that these new Rh and copper complexes (**1–10a**, **Zeol-1b–10b**) can be valuable in the catalysed enantioselective cyclopropanation of styrene and 1,2-dihydropyrene with ethyl and *t*-butyl-diazoacetate. The main product was a mixture of alkyl *cis/trans*-2-cyclopropanecarboxylate. The chemical yield is high (in the range 60–90%). The *cis/trans* selectivity strongly depends on the nature of the catalyst, substrate and diazoacetate. Generally the chemical yields for alkyl *trans*-2-cyclopropanecarboxylate are higher than for the *cis* ester. All complexes were found to induce asymmetric cyclopropanation of alkenes. It must be noted that the stereoselectivity in the reaction products is small but outside error. The magnitude of the small enantioselectivity observed was generally greater with *trans* than the *cis* isomer. The low enantioselectivity is presumably due to the loss of the bidentate coordination of the ligand with the metal because of the opening of the seven-membered ring.

Chemical yields of unsupported and zeolite-supported complexes are almost identical. The zeol-complexes induce a higher proportion of *cis* ester than the soluble catalysts due to geometrical constraints. The supported complexes are stable over prolonged reaction times and presence of traces of oxygen in the feedstock. The activity observed with these supported complexes, plus the fact that prolonged activity can be achieved in a continuous operation without detectable loss of metal from the support, indicates that these are truly heterogeneous counterparts of homogeneous transition metal complex catalysts for cyclopropanation of alkenes.

To summarise, zeolite complexes show interesting catalytic properties in cyclopropanation reactions and these properties are related to the changes in the microenvironment of the ligand–metal complex, caused by the support. These catalysts can be recovered and reused retaining most of their catalytic activity.

Acknowledgements

The authors are grateful for the financial support from Dirección General de Investigación Científica y Técnica (Project MAT94-0359-C02-02, MAT97-1016-C02-02).

References

- [1] M. Elliot, A.W. Farnham, N.F. James, P.H. Needham, A. Pulman, J.H. Stevenson, *Nature* 246 (1973) 169.
- [2] D. Arlt, M. Jantelat, R. Lantzsh, *Angew. Chem. Int. Ed. Engl.* 8 (1981) 719.
- [3] H.N.C. Wong, M.-V. Hon, C.W. Tse, Y.-C. Yip, J. Tanko, T. Hudlicky, *Chem. Rev.* 89 (1989) 165.
- [4] T. Hudlicky, J.W. Reed, in: B.M. Trost (Ed.), *Comprehensive Organic Synthesis*, Vol. 5, Pergamon Press, UK, 1991, p. 989.
- [5] N. Kirmse, *Carbene Chemistry*, 2nd edn., Academic Press, New York, 1971, p. 85.
- [6] D.S. Wulfman, B.W. Peace, R.S. McDaniel Jr., *Tetrahedron* 32 (1976) 1231, 1251.
- [7] S. Patai, *The Chemistry of Diazonium and Diazo Groups*, Wiley, New York, 1978, p. 615.
- [8] M.P. Doyle, *Acc. Chem. Res.* 19 (1986) 348.
- [9] M.P. Doyle, *Chem. Rev.* 89 (1989) 1247.
- [10] M.P. Doyle, in: I. Ojima (Ed.), *Catalytic Asymmetric Synthesis*, VCH Publishers, New York, 1993, p. 63.
- [11] M.P. Doyle, *Recl. Trav. Chim. Pays-Bas* 110 (1991) 305.
- [12] M.P. Doyle, in: L.S. Hegeudus (Ed.), *Comprehensive Organometallic Chemistry II*, Vol. 12, Chap. 5, Pergamon, New York, 1995.
- [13] S.G. Maas, *Top. Curr. Chem.* 137 (1987) 75.
- [14] R.E. Rowenthal, S. Masamune, *Tetrahedron Lett.* 32 (1991) 7373.
- [15] T. Aratani, *Pure Appl. Chem.* 57 (1985) 1839.
- [16] H. Brunner, *Top. Stereochem.* 18 (1988) 129.
- [17] R. Noyori, *Asymmetric Catalysis in Organic Reactions*, Wiley, New York, 1994.
- [18] H. Brunner, W. Zettmeier, *Handbook of Enantioselective Catalysis with Transition Metal*, VCH Publishers, RFA, 1993.
- [19] H. Brunner, *Synthesis* (1985) 645.
- [20] H. Brunner, *Synthesis* (1988) 645.
- [21] K. Smith (Ed.), *Solid Supports and Catalysts in Organic Synthesis*, Ellis Horwood, Chichester, 1992.
- [22] F.R. Hartley, M. Eisen, T. Bernstein, J. Blum, H. Schuman, *J. Mol. Catal.* 43 (1981) 199.
- [23] J.M. Fraile, J.I. García, J.A. Mayoral, *Chem. Commun.* (1996) 1319.
- [24] R.V. Parish, D. Habidi, V. Mohanmadi, *J. Organomet. Chem.* 369 (1989) .
- [25] H. Brunner, E. Bieldmeier, J. Wiehl, *J. Organomet. Chem.* 384 (1990) 223.
- [26] A. Corma, A. Carmona, M. Iglesias, F. Sánchez, *Inorg. Chim. Acta* 244 (1996) 239.

- [27] A. Corma, A. Carmona, M. Iglesias, F. Sánchez, *Inorg. Chim. Acta* 244 (1996) 79.
- [28] A. Corma, A. Carmona, M. Iglesias, A. San José, F. Sánchez, *J. Organomet. Chem.* 492 (1995) 11.
- [29] A. Corma, M. Iglesias, C. Del Pino, F. Sánchez, *J. Organomet. Chem.* 431 (1992) 233.
- [30] L.L. Murrell, in: J.J. Burton, R.L. Garten (Eds.), *Advanced Materials in Catalysis*, Chap. 8, Academic Press, NY, 1977.
- [31] H. Brunner, H. Kluschanzoff, K. Wutz, *Bull. Soc. Chim. Belg.* 98 (1989) 63.
- [32] H. Brunner, K. Wutz, *New J. Chem.* 12 (1992) 57.