Preparation of new chiral dioxomolybdenum complexes heterogenised on modified USY-zeolites Efficient catalysts for selective epoxidation of allylic alcohols

A. Corma [a], A. Fuerte [b], M. Iglesias [c], F. Sánchez [b,*]

[a] *Instituto de Tecnología Química, UPV-CSIC, Avda. de los Naranjos s / n, 46022 Valencia, Spain*
[b] *Instituto de Química Orgánica General, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain*
[c] *Instituto de Ciencia de Materiales, Sede D, CSIC, Serrano 113 bis, 28006 Madrid, Spain*

Abstract

A series of dioxomolybdenum(VI) complexes were synthesised by reaction of Mo(VI) complexes with new chiral ligands derived from (2S,4R)-4-hydroxyproline. The complexes bearing a Si(OEt)$_3$ group were heterogenised to a modified USY-zeolite by covalent bonding. All catalysts, homogeneous and heterogenised, are active and regioselective in the epoxidation of allylic alcohols at room temperature using *tert*-butyl hydroperoxide as terminal oxidant. The catalytic activity of the heterogenised complexes is generally comparable with the corresponding homogeneous ones, yielding epoxyalcohols with excellent yields and selectivity and moderate enantioselectivity. Life time of heterogenised catalysts has been examined by repeated use of the complexes leading similar rates and yields of epoxide, whilst no appreciable loss of metal has been observed over several runs.

1. Introduction

The transition metal-catalysed epoxidation of alkenes using alkyl hydroperoxides as the oxygen source has been extensively employed in the last two decades in both laboratory and industrial processes [1]. In the laboratory Sharpless and Verhoeven have made extensive studies of regio- and stereoselective alkene epoxidations using molybdenum and vanadium-based complexes as catalysts [2], and enantioselective epoxidations of allylic alcohols with *t*-butyl hydroperoxide (TBHP) activated by a titanium-di-

alkyl tartrate (Katsuki–Sharpless reagent) [3]. The most important industrial application is the oxidation of propene: the Halcon or Arco process using homogeneous Mo(VI) [4] or heterogeneous Ti-silica [5] catalysts.

Research on readily recoverable and recyclable supported heterogenised catalysts for oxidative processes has grown steadily in recent years. The majority of these has been based upon polymer supports (specially porous polystyrene resins) [6], and has displayed favourable activity and selectivity, but in terms of recycling, has been disappointingly unstable and often showing excessive metal leaching. These main disadvantages could be overcome by heterogenising the complexes on a high sur-

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face supports (silica or zeolite) [7], which stabilize the Mo-species and the organometallic compound remains strongly bonded to support during reaction course. Heterogenised homogeneous catalysts combine the properties of the homogeneous ones, as reactivity, controllability and selectivity, and the heterogeneous ones, as enhanced stability and reusability [8]. In a previous paper we reported on the synthesis, reactions and catalytic applications of some zeolite-anchored Mo-complexes for epoxidating simple alkenes [9]; the use of zeolite-supported Mo-complexes in oxygen transfer reactions involving TBHP in comparison with the corresponding homogeneous reactions were made.

In this paper we describe the selective synthesis, as pure enantiomers, and characterisation of chiral $MoO_2(acac)L$ where L are bidentate O,O-ligands derived from (L)-trans-4-hydroxy-proline. Those compounds bearing an $Si(OEt)_3$ group were heterogenised by anchoring into modified USY-zeolites. The application of these novel heterogeneous catalysts for the selective epoxidation of allylic alcohols was tested.

2. Experimental

2.1. Materials

Molybdenyl acetylacetonate ($MoO_2(acac)_2$) (Aldrich Chemical) was used as supplied. All solvents were carefully degassed prior to use. The silylating agent $OCN(CH_2)_3Si(OEt)_3$ obtained from Fluka (96%) was distilled before use. An anhydrous solution of TBHP in CH_2Cl_2 recently prepared from aqueous TBHP-70 according to a literature method was employed [2].

All preparations of Mo-complexes were carried out under dinitrogen by standard Schlenk techniques. C, H and N analyses were carried out by the analytical department of the Institute of Organic Chemistry and Institute of Materials Science (C.S.I.C.) with a Heraeus and a Perkin-Elmer 240C apparatus, respectively.

Metal contents were determined by atomic absorption in a Unicam (SP9) Philips apparatus. Infrared spectra were recorded with a Nicolet XR60 spectrophotometer (range 4000–200 cm^{-1}). ^{1}H- and ^{13}C-NMR spectra were taken on Varian XR300 and Bruker 200 spectrometers; chemical shifts are given in ppm with tetramethylsilane as internal standard. Optical rotation values were measured with a Perkin Elmer 241 MC polarimeter.

The inorganic support taken as model is an ultrastable Y zeolite (USY) prepared by steam calcination at 1023 K from a partly (80%) ammonium exchanged NaY (SK40 Union Carbide), followed by treatment with a 1 N citric acid solution at 333 K for 30 min for removing extraframework species. After this, the zeolite was thoroughly washed and dried at 403 K for 6 h. The final zeolite contained, besides the typical ca. 12 Å micropores, a well developed supermicropore–mesopore system (pore diameter 12–30 Å). 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 SiO_2/Al_2O_3, 4.2; crystallinity, > 95%. The inorganic support was dried at 415 K under 0.01 torr before the anchoring process.

2.2. Preparation of the ligands

2.2.1. Methyl (S)-N-benzyl-4-oxopyrrolidine-2-carboxylate (1)

To a solution of oxalyl chloride (1.4 g, 11 mmol) in methylene chloride (25 ml) cooled at −60°C, dimethyl sulphoxide (1.7 g, 22 mmol) in methylene chloride (5 ml) was added during 2 min, then a 2-ml solution of methyl (2S,4R)-N-benzyl-trans-4-hidroxypyrrolidine-2-carboxylate (2.35 g, 9.43 mmol). After stirring for 1 h at −60°C, triethylamine (7 ml, 50 mmol) was added and then allowed to warm up to room

temperature. Water (50 ml) was added and the aqueous layer was extracted with an additional 50 ml of methylene chloride. The organic extracts were washed successively with water (20 ml) and brine (20 ml), dried over $MgSO_4$ and concentrated to dryness. The crude ketone was distilled (130°C/0.3 torr) to yield **1**. Yield: 86%; M.p.:46–47°C. $[\alpha]_D^{25} = -48.1°$ (MeOH, 1). IR (cm^{-1}): ν(COOMe): 1765 (s); ν(C = O): 1750 (s). ^{1}H-NMR (Cl$_3$CD): $\delta = 7.5–7.2$ (m, 5H, arom); 3.85 (m, 1H, CHN); 3.92 (d, 1H, H-5); 3.75 (d, 1H, H-5'); 3.35–3.02 (AB, 2H, CH$_2$Ph); 2.9–2.4 (m, 2H, H-3,H-3').

2.2.2. (2S,4R)-N-benzyl-4-hydroxy-4-phenyl-2-(1,1-diphenylmethyl)pyrrolidinylmethanol (2)

To a 1.8 M solution of PhLi (35.6 ml, 64 mmol) in THF (27 ml), cooled at −60°C, a solution of methyl (S)-N-benzyl-4-oxopyrrolidine-2-carboxylate (**1**) (3 g, 12.8 mmol) in THF (15 ml) were added dropwise with efficient stirring under argon atmosphere. The reaction was monitored by TLC using ethyl acetate–hexane (1:6) as eluent. After 2 h at −60°C the reaction mixture was heated under reflux for 7 h. The reaction mixture was quenched with ammonium chloride and extracted with ethyl ether (150 ml). The organic extracts were successively washed with water (2 × 20 ml) and brine (25 ml) and the solvent evaporated under reduced pressure. The residue was purified by chromatography on silica gel using ethyl acetate–hexane (1:10) as to yield **2**. Yield 68%. M.p.: 203–205°C; $[\alpha]_D^{25} = +67.6$ (methanol, 1). IR (cm^{-1}): ν(CC-cycl.): 1500 (s), 1450 (s); ν(OH): 3460 (s). ^{1}H-NMR (Cl$_3$CD): $\delta = 7.8–6.7$ (m, 20H, arom); 4.27 (dd, 1H, CHN); 3.60 (s, 1H, OH); 3.20–3.03 (AB, 2H, CH$_2$Ph); 3.10 (d, 1H, H-5); 3.03 (d, 1H, H-5'); 2.64 (dd, 1H, H-3); 2.09 (m, 1H, H-3').

2.2.3. (2S,4S)-N-benzyl-4-hydroxy-4-phenyl-2-(1,1-diphenylmethyl)pyrrolidinylmethanol (3)

In a flamed flask was poured into magnesium (925 mg, 38.1 mmol) and THF (75 ml) in argon atmosphere under ultrasound irradiation, a solu-

tion of bromobenzene (5.6 g, 38.1 mmol) in THF (10 ml) was dropwise added; the irradiation was maintained for 2 h. After the magnesium reacted a solution of methyl (S)-N-benzyl-4-oxopyrrolidine-2-carboxylate (**1**) (3 g, 12.8 mmol) in THF (5 ml) was added dropwise and the reaction mixture was heated under reflux for 16 h. The reaction mixture was cooled, quenched with a saturated solution of ammonium chloride (if magnesium hydroxide precipitated, solid NH$_4$Cl was added) and extracted with ethyl ether (150 ml). The organic extracts were successively washed with water (2 × 20 ml) and brine (25 ml) and the solvent evaporated under reduced pressure to yield a mixture of two diastereomers (70%) **9:10** (ratio 30/70). The diastereomeric mixture was chromatographed on silica gel using ethyl acetate: hexane (1:10) as eluent to yield **2** ($R_f = 0.35$; 600 mg) and **3** (Rf = 0.22; 2.10 g). An analytical sample of **3** were obtained for recrystallising from methanol–water (3:1). M.p.: 200–203°C; $[\alpha]_D^{25} = +31.5°$ (MeOH, 1). IR (cm^{-1}): ν(CC-cycl): 1495 (s), 1450 (s); ν(OH): 3440 (s). ^{1}H-NMR (Cl$_3$CD): $\delta = 7.9–6.9$ (m, 20H, arom); 5.2 (s, 1H, OH); 4.73 (dd, 1H, CHN), 3.7–3.4 (AB, 2H, CH$_2$Ph); 3.28 (dd, 1H, H-5); 2.95 (dd, 1H, H-5'); 2.3–2.0 (m, 2H, H-3, H-3').

2.2.4. (2S,4R)-4-hydroxy-4-phenyl-2-(1,1-diphenylmethyl)pyrrolidinylmethanol (4)

A mixture of (2S,4R)-N-benzyl-4-hydroxy-4-phenyl-2-(1,1-diphenylmethyl) pyrrolidinylmethanol (**2**) (500 mg, 1.15 mmol) in ethanol (89 ml), sulphuric acid (64 μl, 1.15 mmol) and Pd(OH)$_2$/C (124 mg) was hydrogenated at 15 atm until removing the benzyl group (TLC). The reaction mixture was filtered and treated with concentrated sodium hydroxide solution until pH 11–12, with vigorous stirring. The water was removed by azeotropic distillation with acetonitrile under reduced pressure. The residue was chromatographed on silica gel using CH$_2$Cl$_2$ as eluent. Yield 76%. M.p.: 65–68°C; $[\alpha]_D^{25} = +17.8°$ (MeOH, 1). IR (cm^{-1}): ν(CC-cycl): 1490 (s), 1450 (s); ν(OH): 3350. ^{1}H-NMR

(Cl$_3$CD): $\delta = 7.6$–7.0 (m, 15H, arom); 4.52 (dd, 1H, CHN); 3.17–3.07 (AB, 2H, H-5, H-5′); 2.20 (dd, 1H, H-3); 1.91 (dd, 1H,H-3′).

2.2.5. (2S,4S)-4-hydroxy-4-phenyl-2-(1,1-di-phenylmethyl)pyrrolidinylmethanol (5)

Following the procedure for **4**, the amino–alcohol **5** was obtained starting from (2S,4S)-N-benzyl-4-hydroxy-4-phenyl-2-(1,1-diphenyl-methyl)pyrrolidinylmethanol (**3**) (3.1 g, 7 mmol) and Pd/C (600 mg). Yield 100%. M.p. = 160–161°C; $[\alpha]_D^{25} = -16.6°$ (MeOH, 1). IR (cm^{-1}): ν(CC-cycl): 1495 (s), 1450 (s); ν(OH, NH): 3390 (s). ^{1}H-NMR (DMSO-d$_6$-500 MHz): $\delta = 7.6$–7.0 (m, 15H, arom); 5.03 (t, 1H, NH); 4.05 (m, 1H, CHN); 3.05 (m, 1H, H-5); 2.75 (m, 1H, H-5′); 2.21 (m, 1H, H-3); 1.79 (m, 1H, H-3′).

2.2.6. (2S,4R)-N-t-butylaminocarbonyl-4-hydroxy-4-phenyl-2-(1,1-diphenylmethyl)pyrrolidinyl methanol (6a)

To a solution of (2S,4R)-4-hydroxy-4-phenyl-2-(1,1-diphenylmethyl)pyrrolidinyl-methanol (**4**) (65 mg, 0.19 mmol) in methylene chloride (50 ml), cooled in an ice-bath a solution of t-butylisocyanate (22 ml, 0.19 mmol) was added dropwise with efficient stirring under argon atmosphere. The reaction was monitored by t.l.c using ethyl acetate as eluent, after the reaction was completed (1 h) the solvent was evaporated under reduced pressure to yield **6a**. Yield: 100%.

M.p.: 185–187°C; $[\alpha]_D^{25} = +234.9°$ (MeOH, 1). IR (cm^{-1}): ν(NC=ON): 1645 (s), 1510 (s); ν(CC-cycl): 1495 (s), 1450 (s); ν(OH, NH): 3420 (s). ^{1}H-NMR (Cl$_3$CD): $\delta = 7.6$-7.1 (m, 15H, arom); 5.30 (s, 1H, NH); 5.02 (dd, 1H, CHN); 4.19–3.62 (AB, 2H, H-5, H-5′); 2.60 (dd, 1H, H-3); 2.26 (dd, 1H, H-3′); 0.99 (s, 9H, CCH$_3$).

2.2.7. (2S,4S)-N-t-butylaminocarbonyl-4-hydroxy-4-phenyl-2-(1,1-diphenylmethyl)pyrrolidinyl methanol (7a)

Following the procedure for **6a**, the compound **7a** was obtained starting from (2S,4S)-4-hydroxy-4-phenyl-2-(1,1-diphenylmethyl)pyrrolidinylmethanol (**5**) (200 mg, 0.6 mmol) and tert-buthylisocyanate (60 mg, 0.6 mmol). Yield: 100%. M.p.: 180–183°C; $[\alpha]_D^{25} = +56.6°$ (MeOH, 1). IR (cm^{-1}): ν(NC=ON): 1630 (s), 1530 (s); ν(CC-cycl): 1495 (s), 1450 (s); ν(OH, NH): 3400 (s). ^{1}H-NMR (DMSO-d$_6$): $\delta = 7.8$–7.4 (m, 15H, arom); 5.80 (s, 1H, NH); 5.33 (m, 1H, CHN); 4.10 (d, 1H, H-5); 3.21(d, 1H, H-5′); 2.5–2.3 (m, 2H, H-3, H-3′); 1.38 (s, 9H, CCH$_3$).

2.2.8. (2S,4R)-N-(-3-triethoxysilyl)propyla-minocarbonyl-4-hydroxy-4-phenyl-2-(1,1-di-phenylmethyl)pyrrolidinylmethanol (6b)

Following the procedure for **6a** starting from (2S,4R)-4-hydroxy-4-phenyl-2-(1,1-diphenyl-methyl)pyrrolidinylmethanol (**4**) (144 mg, 0.42
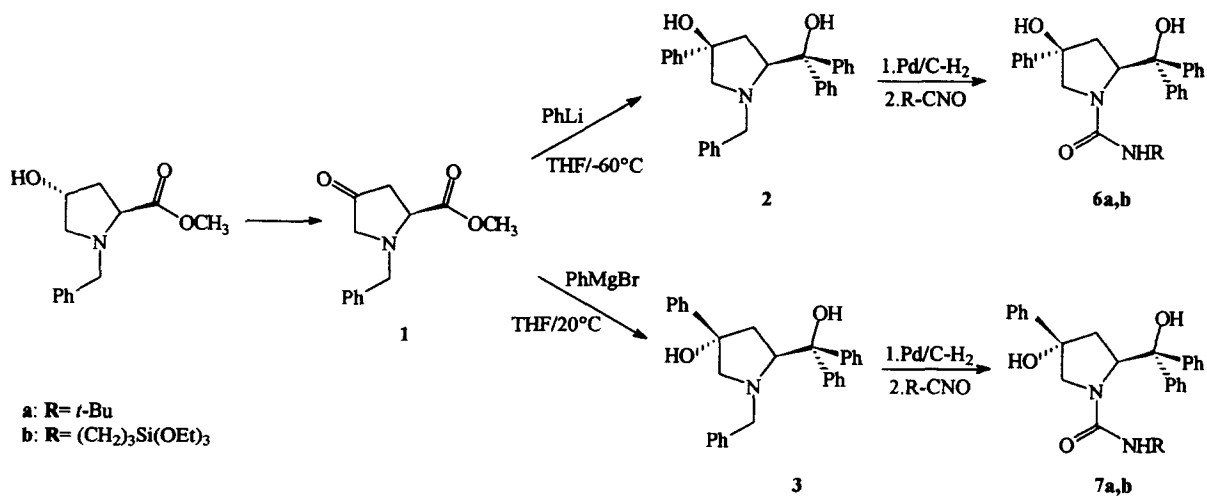
Table 1
Physical properties of dioxomolybdenum complexes

Compound Mo O$_2$(acac)L	Elemental analysis (found (calc.)(%))				$[\alpha]_D^{25}$	Yield
	C	H	N	Metal	(Solvent, c)	(%)
8a	64.46	5.17	2.00	15.08	−78.0°	84
(L = **2**)	(64.43)	(5.18)	(2.11)	(14.79)	EtOH, 0.5	
9a	63.48	4.68	1.73	15.06	−103.5°	76
(L = **3**)	(63.43)	(5.18)	(2.11)	(14.79)	MeOH, 0.5	
8b	58.93	5.94	3.89	15.21	−294.3°	82
(L = **6a**, R = C(CH)$_3$)	(59.00)	(5.56)	(4.17)	(14.59)	CH$_2$Cl$_2$, 0.25	
9b	58.54	5.87	4.35	15.00	−158.8°	85
(L = **7a**, R = C(CH)$_3$)	(59.00)	(5.56)	(4.17)	(14.59)	CH$_2$Cl$_2$, 0.25	
8c	55.89	5.55	3.42	12.21	−97.7°	79
(L = **6b**, R = (CH$_2$)$_3$Si(OEt)$_3$)	(55.66)	(6.03)	(3.42)	(11.9)	CH$_2$Cl$_2$, 0.25	
9c	56.00	6.00	3.51	12.00	−104.0°	81
(L = **7b**, R = (CH$_2$)$_3$Si(OEt)$_3$)	(55.66)	(6.03)	(3.42)	(11.9)	CH$_2$Cl$_2$, 0.25	

Table 2
Spectroscopic data of dioxomolybdenum complexes

Compound	IR (cm^{-1})	^{1}H-NMR (δ, ppm)
8a (L = 2)	ν(Mo=O): 940, 900	7.6–6.9 (20 H, Ph); 5.4 (1H, CH, acac); 4.8 (1H, CHN); 4.4, 3.0 (2H, AB, J = 10.4 Hz, CH$_2$N); 4.2, 4.0 (2H, AB, J = 14.1 Hz, CH$_2$Ph); 2.4–2.1 (m, 2H, CH_2CH); 2.0 (s, 6H, CH$_3$, acac)
9a (L = 3)	ν(Mo=O): 950, 910	7.8–7.1 (20H, Ph); 5.4 (1H, CH, acac); 4.9 (1H, CHN); 3.4 (2H, dd, AB, J = 13.2 Hz, CH$_2$-Ph); 3.1–2.8 (2H, CH$_2$N); 2.2 (1H, CH_2-CH); 2.1 (1H, CH_2-CH); 1.9 (s, 6H, CH$_3$, acac)
8b (L = 6a, R = C(CH$_3$)$_3$)	ν(NH): 3440 ν(CO): 1650 ν(Mo=O): 940, 910	7.5–7.1 (15H, Ph); 5.40 (1H, CH, acac); 5.1 (1H, CHN); 4.20 (1H, d, J = 11.5, CH$_2$N); 3.6–3.5 (1H, CH$_2$N); 2.6 (dd, 1H, J = 9.0, 14.3, -CH_2CH-); 2.3–2.1 (m, 1H, -CH_2CH-); 2.1 (s, 6H, CH$_3$, acac); 1.0 (s, 9H, ^{t}Bu)
9b (L = 7a, R = C(CH$_3$)$_3$)	ν(NH): 3420 ν(CO): 1600 ν(Mo=O): 940, 910	7.7–7.1 (15H, Ph); 5.48 (s, 1H, acac); 5.3–5.1 (m, 1H, CHN); 4.0–3.6 (m, 2H CH$_2$N); 2.6–2.2 (m, 2H, -CH_2CH); 2.1 (s, 6H, CH$_3$, acac); 1.2 (s, 9H, ^{t}Bu)
8c (L = 6b, R = (CH$_2$)$_3$Si(OEt)$_3$)	ν(NH): 3400 ν(CO): 1600 ν(Mo=O): 940, 910	7.7–7.1 (m, 15H, arom); 5.40 (1H, CH, acac); 5.12 (dd, 1H, CHN); 4.15–3.60 (AB, 2H, CH$_2$N); 3.73 (q, 6H, CH$_2$OSi); 2.90–2.71 (m, 2H, CH$_2$N); 2.50 (dd, 1H, H-3); 2.20 (dd, 1H, H-3′); 2.1 (s, 6H, CH$_3$, acac); 1.29–1.11 (m, 2H, CCH$_2$C); 1.15 (t, 9H, CCH$_3$); 0.39 (m, 2H, CH$_2$Si)
9c (L = 7b, R = (CH$_2$)$_3$Si(OEt)$_3$)	ν(NH): 3410 ν(CO): 1605 ν(Mo=O): 940, 910	7.6–7.0 (m, 15H, arom); 5.48 (s, 1H, acac); 5.2 (m, 1H, CHN); 4.1–3.5 (m, 2H, CH$_2$N); 3.7–3.6 (m, 6H, CH$_2$OSi); 2.90–2.71 (m, 2H, CH$_2$N); 2.5–2.3 (m, 2H, CH_2CH); 2.1 (s, 6H, acac); 1.3–1.1; (m, 2H, CCH$_2$C); 1.1 (m, 9H, CCH3); 0.4 (m, 2H, CH$_2$Si).

mmol) and 3-triethoxysilylpropylisocyanate (109 mg, 0.42 mmol) after 6 h, the compound 6b was obtained. Yield: 72%; M.p.: 51–52°C; $[\alpha]_D^{25}$ = +72.3° (MeOH, 1). IR (cm^{-1}): ν(NC=ON): 1620 (s), 1530 (s); ν(CC-cycl): 1495 (s), 1450 (s); ν(OH, NH): 3400 (s). ^{1}H-NMR (Cl$_3$CD): δ = 7.6–7.1 (m, 15H, arom); 5.72 (s, 1H, NH); 5.00 (dd, 1H, CHN); 4.13–3.61 (AB, 2H, H-5,

Scheme 1. Scheme 1.

Table 3

Analytical data for the heterogenised complexes on a modified zeolite USY

Catalyst	% anchored	Analysis (found (%))			Mo=O	
		C	H	N	M	IR bands/cm^{-1}
Zeol-8c	93	5.34	2.23	0.55	1.06	940, 910
Zeol-9c	90	4.64	2.06	0.63	0.95	940, 910

H-5'); 3.73 (c, 6H, CH$_2$OSi); 2.93–2.61 (m, 2H, CH$_2$N); 2.57 (dd, 1H, H-3); 2.28 (dd, 1H, H-3'); 1.29–1.11 (m, 2H, CCH$_2$C); 1.15 (t, 9H, CCH$_3$); 0.39 (m, 2H, CH$_2$Si).

2.2.9. (2S,4S)-N-(-3-triethoxysilyl)propylaminocarbonyl-4-hydroxy-4-phenyl-2-(1,1-diphenylmethyl)pyrrolidinylmethanol (7b)

Following the procedure for **6a** starting from (2S,4S)-4-hydroxy-4-phenyl-2-(1,1-diphenylmethyl)pyrrolidinylmethanol (**5**)) (400 mg, 1.2 mmol) and 3-triethoxysilylpropylisocyanate (300 mg, 1.2 mmol) was obtained after 6 h the compound **9**. Yield: 100%; $[\alpha]_D^{25} = +42.5°$ (MeOH, 0.55). IR (cm^{-1}): ν(NC=ON): 1610 (s), 1535 (s); ν(CC-cycl): 1495 (s), 1450 (s); ν(OH, NH): 3380 (s). ^{1}H-NMR (C$_6$D$_6$) $\delta =$ 7.8–7.0 (m, 15H, arom); 5.40 (m, 1H, CHN);

3.85 (q, 6H, CH$_2$OSi); 3.77 (d, 1H, H-5); 3.20 (m, 2H, CH$_2$N); 2.70 (m, 1H,H-5'); 2.45 (m, 1H, H-3); 2.35 (m, 1H, H-3'); 1.25–1.20 (m, 2H, CCH$_2$C); 1.18 (s, 9H, CCH$_3$); 0.64 (m, 2H, CH$_2$Si).

2.3. Preparation of dioxomolybdenum complexes

2.3.1. General procedure

A solution of the corresponding ligand **2–7** (0.43 mmol) in methylene chloride or cyclohexane (10–15 ml) was added dropwise to a stirred solution of MoO$_2$(acac)$_2$ (139 mg, 0.43 mmol) in the same solvent 50 ml in Schlenk type flask under argon atmosphere. The reaction mixture was stirred for 1–5 h at r.t. (CH$_2$Cl$_2$, ligands **2**, **6a**, **6b**) or 70°C (cyclohexane, ligands **3**, **7a**, **7b**). The solid crude complex was filtered, washed with ethyl ether or hexane. Characterisation of the different complexes has been carried out by elemental analysis of C, H, N, atomic absorption of Mo, and ^{1}H-NMR and IR spectra. The experimental physical and spectroscopic data are given in Tables 1 and 2, respectively.

Table 4

Catalytic epoxidation of allylic alcohols with TBHP using homogeneous and zeolite-heterogenised Mo catalysts (0.5% mol) [a] at room temperature

Catalyst	Geraniol				Nerol			
	Time (h)	Conv. (%) [b]	Select. (%) [c]	ee (%) [d,e]	Time (h)	Conv. (%) [b]	Select. (%) [c]	ee (%) [d,f]
8a	4	93	92	4.8	1	93	92	2.4
8b	4	40	92	12	5	60	94	5
Zeol-8c	4/18	40/82	99	–	5	78	98	–
9a	4	94	93	3.4	4	91	92	–
9b	4	80	91	27.6	4	94	92	10.4
Zeol-9c	4/8	75/90	96	47	3	98	99	64

[a] Based on molybdenum.
[b] Conversion of allylic alcohol.
[c] Percentage of β,γ-epoxyalcohol in the products.
[d] Measured by GLC on a permethyl β-cyclodextrine/OV-701 (15/85) column.
[e] 2S,3S-epoxigeraniol.
[f] 2S,3R-epoxinerol.

2.4. Preparation of zeolite heterogenised molybdenum complexes

A molybdenum-complex bearing a triethoxysilyl group (0.2 mmol), described above, in dry dichloromethane (2 ml) was added to a suspension of the inorganic support (modified USY-zeolite dried at 140°C for 3–4 h 'in vacuo') (1 g) in dry toluene (40 ml) (Scheme 1). The mixture was stirred, under argon, for 24 h at room temperature. Then, the solid was filtered and Soxhlet-extracted with CH_2Cl_2/ethyl ether (1:1) for 7 h to remove the remaining non-supported complex. The pale solid was dried in vacuo. The structure of the supported complex was deduced from analytical and spectroscopic data. The co-ordination sphere around the metal is the same for the unsupported complexes under these reaction conditions. The analytical data were presented in Table 3.

2.5. Catalytic epoxidation of allylic alcohols

A typical procedure for the epoxidation of allylic alcohols is as follows: into a 25-ml round-bottomed flask catalyst (0.0048 mmol), CH_2Cl_2 (2.5 ml), alkene (1 mmol) was placed and TBHP solution (1.5 mmol anhydrous solution in CH_2Cl_2) was added dropwise, this point being taken as the starting of the reaction. Samples were periodically withdrawn by syringe during the reaction period and monitored by GLC on a permethyl-β-cyclodextrine/OV-701 (15/85) capillary column by comparison with authentic samples. The results obtained are summarised in Table 4.

3. Results and discussion

3.1. Synthesis of ligands and catalysts

The chiral dihydroxy ligands were prepared from methyl (2S,4R)-N-benzyl-4-oxopyrrolidine-2-carboxylate [9]. The attack to the 4-keto group can be done highly selective by tuning the temperature and nature of organometallic reagent, yielding almost exclusively the enantiomerically pure (2S,4R) or (2S,4S)-proline derivatives 2, 3 depending of the conditions given (Scheme 1).

The introduction of N-carbamoyl substituents containing a t-butyl group, useful for working in solution, or a triethoxysilyl group, adequate for anchoring on zeolite, was performed by treatment of free amine with the selected alkylisocyanate at room temperature in quantitative yields. In preparation of ureas 6b and 7b, bearing a triethoxysilyl group, no products from hydrolysis of Si–OEt bonds in the reaction media could be detected.

The molybdenum complexes were prepared by using a ligand exchange procedure, in which

a: R= CH2Ph
b: R= CONH-tBu
c: R= CONH-(CH2)3Si(OEt)3

8a-c, 9a-c

Zeol-8c, Zeol-9c
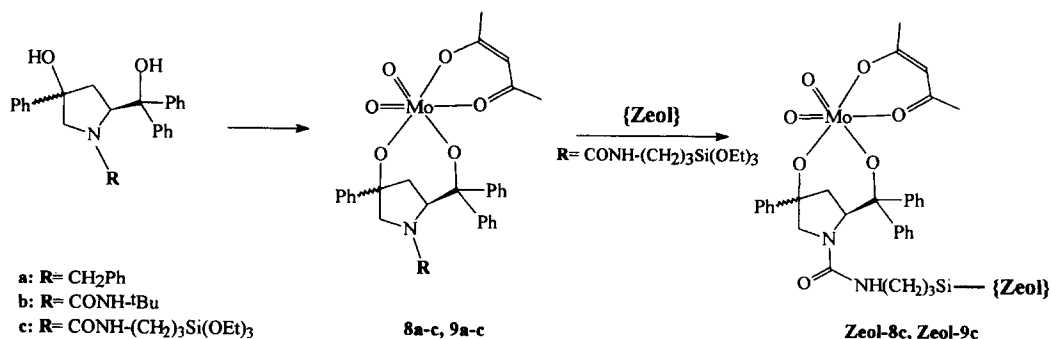
Scheme 2. Scheme 2.

ligands were reacted with $MoO_2(acac)_2$ in the stoichiometric ratio at r.t. or 60°C. The resulting complex were isolated by crystallization in excellent yields. In all cases the IR spectra contained two bands assigned to Mo=O stretching modes in the region 950–900 cm^{-1} as well as bands which belong to acetylacetonate group and the corresponding chiral ligand. The structure of the products were determined by spectroscopic methods and elemental analysis (C, H, N, Mo) (Scheme 2).

The complexes bearing the $Si(OEt)_3$ were

bonded covalently to the free silanols in the support (USY-zeolite) at room temperature by controlled hydrolysis of ethoxysilyl group and posterior reaction with superficial silanols. The successful synthesis of the supported catalysts is confirmed by the analytical data of C, H, N and atomic adsorption of molybdenum with good loading ∼ 1% (more than adequate for catalytic applications) were achieved. In all cases the IR spectra show bands at 940 and 910 cm^{-1} assigned to two cis-Mo=O stretching modes, indicating the presence of oxo-molybdenum cen-
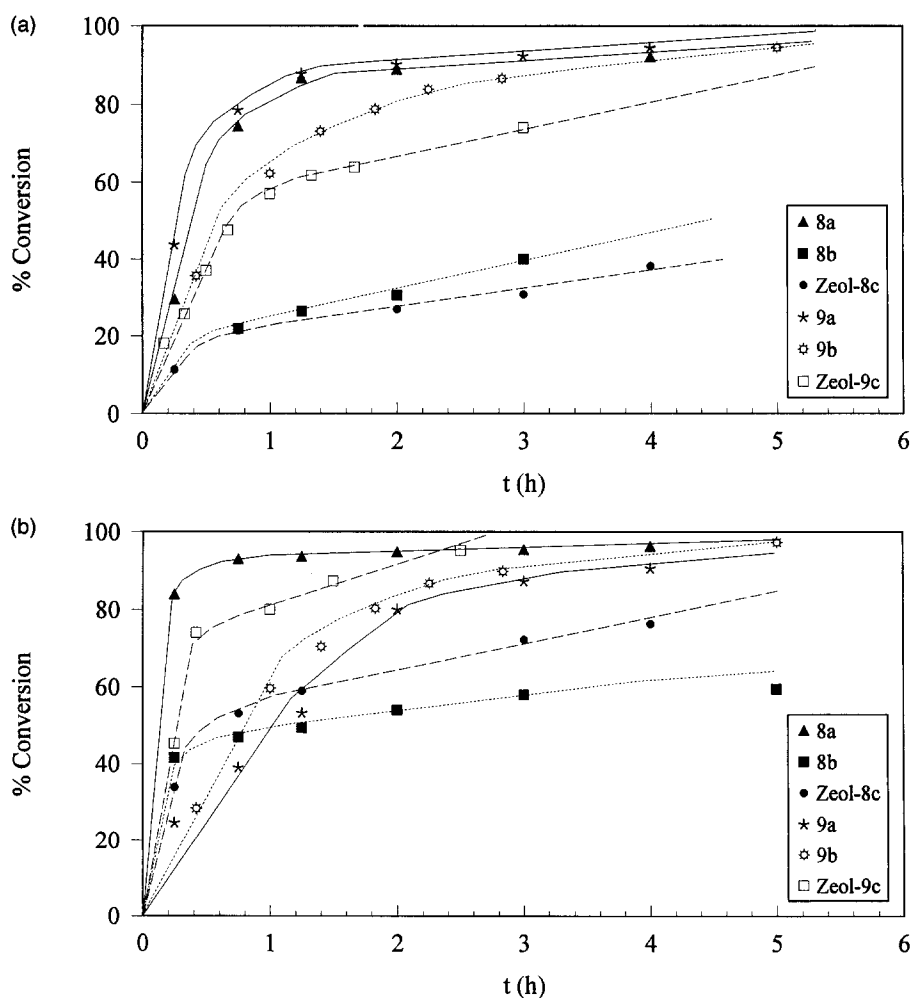

Fig. 1. (a) Kinetic profile of epoxidation of geraniol with several Mo-catalysts. (b) Kinetic profile of epoxidation of nerol with several Mo-catalysts.

ters on the surface. The catalysts also showed evidence in the IR spectrum for the retention of an acac ligand.

3.2. Epoxidation of allylic alcohols

The soluble and heterogenised Mo-complexes were tested for the epoxidation of (E)- and (Z)-3,7-dimethyl-2,6-octadien-1-ol (geraniol and nerol, respectively), which were used as models, with TBHP as oxygen source at room temperature, 0°C and −20°C in anhydrous conditions. The results of epoxidation of allylic alcohols are summarised in Table 4.

Even though for test reactions we have only used 0.5% of molar ratio catalysts/substrate the conversion of allylic alcohols is generally high. The selectivity of the reaction toward the formation of 2,3-epoxialcohols obtained with homogeneous and zeolite-supported catalysts was almost complete (up to 99%) with both types of catalysts. The time-course plots of the epoxidation of geraniol and nerol catalysed by homogeneous and heterogenised Mo-complexes are shown in Fig. 1. The results obtained for heterogenised catalysts are generally comparable with the corresponding soluble molybdenum complexes which show a similar pattern indicating that both reactions take place through the same mechanism, without any significant change in the reaction pathway.

The lifetimes of the zeolite catalysts were examined by their repeated use in the epoxidation of geraniol. The amount of metal ion was determined for each run. Approximately more than 95% of the metal was still retained on the zeolite-complex after five runs. The yield of epoxide decreased only slightly (more than 90% remained) and notable change in selectivity has not been observed.

The major advantages of zeolite-anchored catalysts over their homogeneous counterparts are the ease of the recovering and recycling of the catalysts and the easier workup procedure, that permits removing catalysts (metal and chiral inductor) from reaction media through a simple filtration. Our catalysts systems have relatively long lifetime as catalytic activities after five runs are essentially the same as those of the first run. The enhanced stability of the present complexes may be attributed to the stronger co-ordination of the dihydroxyligand to Mo than that of the acetylacetonate or hydroxyl group present on the substrate, t-butylalcohol or hydroperoxide, and by dispersion the molecules of catalysts on the mesopores that avoid the dimerization and polymerization of Mo species.

As it has been claimed earlier for the homogeneous catalysts systems, the high regioselectivity achieved in the epoxidation of allylic alcohols can be interpreted by a mechanism in which simultaneous co-ordination of the hydroxyl groups of the substrate and t-BuOOH to the metal ion at neighboring position is involved in the key intermediate. The fixed geometry of the allylic alcohols by the formation of such ternary complex results in preferential transfer of oxygen to an olefinic site close to the hydroxyl group. This may be supported by the observation that the rate of epoxidation is retarded in the presence of a large amount of t-BuOOH which could compete with the substrate for the co-ordination to the active center.

The enantioselectivity of the reactions are low, except for catalyst **9b** and its corresponding supported **Zeol-9c**. In these catalysts the enantioselectivity increased significantly when moving from homogeneous to heterogenised catalysts, which suggests an important role for the steric constraints of the support. These constraints determine that both ternary diastereoisomeric key intermediates (organometallic complex + substrate + hydroperoxide) must be accommodated differently in the confined spaces of mesopores, where the metal complexes are anchored, and as a consequence, induce a preferential transfer of oxygen to the pro-S face of the olefinic bond.

The high activity and selectivity and the significantly easier workup indicate that this type of catalysts is a truly heterogeneous counterpart of homogeneous transition metal complex cata-

lysts for epoxidation of allylic alcohols in synthetic purposes and large scale operations. Additional efforts are being done for designing and preparing new chiral ligands in order to increase the enantioselectivity.

Acknowledgements

References

[1] R.A. Sheldon, J. Mol. Catal., 20 (1983) 1.
[2] K.B. Sharpless and T.R. Verhoeven, Aldrichim. Acta, 12 (1979) 63.
[3] (a) T. Katsuki and K.B. Sharpless, J. Am. Chem. Soc., 102 (1980) 5974; (b) R.A. Johnson and K.B. Sharpless, in R. Noyori (Ed.), Asymmetric Catalysis in Organic Synthesis, Wiley, New York, 1994, pp. 105–150 and references therein.
[4] (a) J. Kollar, US Pat., 3 350 422, 1967; 3 357 635, 1967; 3 507 809, 1970; 3 625 981, 1971; (b) R. Landau, G.A. Sullivan and D. Brown, Chem. Tech., (1979) 602.
[5] (a) H.P. Wulff, BR Pat., 1 249 079, 1971; US Pat., 3 923 843, 1975; (b) R.A. Sheldon, J. Mol. Catal., 7 (1980) 107.
[6] (a) D.C. Sherrington, Pure Appl. Chem., 60 (1988) 401; (b) M.J. Farral, M. Alexis and M. Trecarten, Nouv. J. Chim., 7 (1983) 449.
[7] (a) F.R. Hartley, M. Eisen, T. Bernstein, J. Blum and H. Schuman, J. Mol. Catal. 43 (1981) 199; (b) F.R. Hartley, Supported metal complexes, D. Reidel, Dordrecht, 1985; (c) F.R. Hartley, in F.R. Hartley (Ed.), The Chemistry of the Metal Carbon Bond, Vol. 4, Wiley, New York, 1987, p. 1164.
[8] (a) U. Nagel and E. Kinzel, J. Chem. Soc. Chem. Comm., (1986) 1089; (b) A. Corma, C. dell Pin, M. Iglesias and F. Sánchez, J. Chem. Soc. Chem. Commun., (1991) 1253.
[9] A. Corma, M. Iglesias, J.R. Obispo and F. Sánchez, in G. Jannes and V. Dubois (Eds.), Chiral Reactions in Heterogeneous Catalysis, Plenum, New York, 1994.