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Synthesis and catalytic properties in olefin epoxidation of chiral oxazoline dioxomolybdenum(VI) complexes

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Abstract

Dioxomolybdenum(VI) complexes with the general formula $[MoO_2X_2(N,N)]$ (X = Cl, $OSiPh_3$) containing a chiral bidentate oxazoline ligand (N,N = 2,2′-bis[(4*S*)-4-benzyl-2-oxazoline]) have been prepared and characterised by ^{1}H NMR, IR spectroscopy and thermogravimetric analysis. The bis(chloro) complex was heterogenised in the ordered mesoporous silica MCM-41 by direct grafting in dichloromethane. Elemental analysis and ^{29}Si MAS NMR spectroscopy of the derivatised material indicated the presence of monopodally anchored species of the type $MoO_2[(-O)_3SiO]Cl(N,N)$. The complex $[MoO_2Cl_2(N,N)]$ and the derivatised material exhibited initial activities of 147 and 255 mol mol_{Mo}^{-1} h^{-1}, respectively, in the catalytic epoxidation of cyclooctene using *tert*-butylhydroperoxide (*t*BuOOH) as the oxidant, both yielding 1,2-epoxycyclooctane quantitatively within 24 h at 55 °C. The MCM-41 grafted catalyst could be recycled with no loss in performance with respect to the epoxide yields obtained for reaction times above 2 h. With *trans*-β-methylstyrene as the substrate, the bis(chloro) complex and the derivatised material gave epoxides as the only products with yields in the range of 56–64% after 24 h, but no catalytic asymmetric induction was observed. The triphenylsiloxy complex was more active than the bis(chloro) complex for the epoxidation of *trans*-β-methylstyrene, but the enantiomeric excess was negligible and the corresponding diols were also formed. For the reaction catalysed by the supported material, changing the oxidant from *t*BuOOH to cumene hydroperoxide greatly improved the catalytic activity but the enantiomeric excess continued very low and the corresponding diol was the main product.

Keywords: Molybdenum; Oxide complexes; Chiral ligands; Oxazoline; Epoxidation; Mesoporous materials

1. Introduction

The enantioselective epoxidation of olefins is an important reaction in the synthesis of fine chemicals and pharmaceuticals [1,2]. Considerable progress has been made using transition metal catalysts bearing chiral ligands [3,4]. The success of molybdenum(VI) complexes in reactions to produce racemic epoxides led to the belief that some derivatives of these complexes could be applied as chiral catalysts [5,6]. Research has focused on the synthesis of chiral monometallic complexes with the $[MoO_2]^{2+}$ core bearing bidentate, tridentate or tetradentate N, O, S-ligands derived from pyridyl alcohols [7–13], oxazolines and bis(oxazolines) [10,14,15], sugar derived Schiff bases [16], oximes, *cis*-diols and 8-phenylthiomenthols [17], tetradentate salen ligands [13,18], and diazabutenes [19]. The enantiomeric excesses obtained for the epoxidation of unfunctionalised olefins using these complexes as catalysts are typically in the range of 20–40%. A limited number of reports also feature the heterogenisation of chiral dioxomolybdenum(VI) complexes on solid supports. For example, the tethering of chiral complexes with bidentate O,O-ligands to the internal surface of a mesoporous USY-zeolite gave a catalyst for the asymmetric epoxidation of

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allylic alcohols [20]. Optically active molybdenum(VI) dioxo complexes bearing hydrosalen derivatives as ligands were also grafted on the surfaces of ordered mesoporous silicas [21]. The heterogenised complexes were found to be applicable for asymmetric epoxidation of *trans*-β-methylstyrene and *cis*-β-methylstyrene with enantiomeric excesses of up to 31% at conversions of up to 55% at room temperature.

Of the chiral ligands mentioned above, oxazolines and bis(oxazolines) have been frequently used in metal-catalysed asymmetric organic transformations [22–26]. In the field of oxomolybdenum(VI) chemistry, complexes of the type $[MoO_2Cl_2(N,N)]$ bearing C_2-symmetric bis(oxazolines) (N,N) were prepared and evaluated as catalysts for the asymmetric epoxidation of *trans*-β-methylstyrene by *t*BuOOH [10]. The complexes showed good catalytic activities (up to 86% conversion after 4 h reaction) but had very low enantiomeric excesses (4–6%). Soon afterwards, Teruel and co-workers described complexes of the type $[MoO_2(N,O)_2]$ containing chiral phenolatooxazoline ligands (N,O) [14]. Using styrene as a substrate, toluene as solvent and *t*BuOOH as the oxidant conversions of 25–29% could be reached within 18 h at 35 °C. The selectivity towards the epoxide was, however, low (<50%) and the enantiomeric excess negligible (ca. 2%). Kandasamy et al. also synthesised two dioxomolybdenum(VI) complexes containing bidentate oxazoline ligands, similar or identical to those described by Teruel and co-workers [15]. Tested in catalysis at room temperature, the performance of the Mo^{VI} catalyst, however, was not good. In further work, Brito et al. reported that the good activity and low diastereoselectivity (with (*R*)-limonene as the substrate) of oxazoline ligated complexes originate from the lability of the two oxazoline ligands, not being strongly attached to the metal centre. Oxazolinylpyridine ligands, found to be non-labile, were described as enabling a better stereoselective control in the catalysed organic reaction [27].

In this paper, we describe the synthesis and characterisation of new chiral dioxomolybdenum(VI) complexes containing a bis(oxazoline) ligand (N,N = 2,2′-bis[(4*S*)-4-benzyl-2-oxazoline]) of the general formula $[MoO_2X_2(N,N)]$ (X = Cl, $OSiPh_3$), the immobilisation of the complex $[MoO_2Cl_2(N,N)]$ in the ordered mesoporous silica MCM-41, and an evaluation of the catalytic properties of the different systems in olefin epoxidation processes using *t*BuOOH as the oxidant.

2. Experimental

2.1. Materials and methods

Powder X-ray diffraction (XRD) data were collected on a Philips X'pert diffractometer using Cu Kα radiation filtered by Ni (λ = 1.5418 Å). Nitrogen adsorption–desorption isotherms were measured at −196 °C, using a gravimetric (subatmospheric) adsorption apparatus equipped with a CI electronic MK2-M5 microbalance and an Edwards Barocel pressure sensor. Before analysis, pristine calcined MCM-41 was degassed at 200 °C and the modified material at 150 °C (to minimise destruction of the functionalities). Thermogravimetric analysis (TGA) was carried out using a Shimadzu TGA-50 system at a heating rate of 5 °C min^{-1} under air. Microanalyses were performed at the Mikroanalytisches Labor of the TU München in Garching (by M. Barth and co-workers).

IR spectra were obtained by the KBr pellet method using a FTIR Mattson-7000 infrared spectrophotometer. ^1H NMR spectra were obtained using a Bruker CXP 300 spectrometer. ^{29}Si solid-state magic-angle-spinning (MAS) NMR spectra were recorded at 79.49 MHz on a Bruker Avance 400 spectrometer. ^{29}Si MAS NMR spectra were recorded with 40° pulses, spinning rates of 5.0–5.5 kHz and 60 s recycle delays. ^{29}Si CP MAS NMR spectra were recorded with 5.5 μs ^1H 90° pulses, 8 ms contact time with a spinning rate of 5 kHz and 4 s recycle delays. Chemical shifts are quoted in parts per million from tetramethylsilane.

All preparations and manipulations were carried out using standard Schlenk techniques under nitrogen. Solvents were dried by standard procedures (*n*-hexane, diethyl ether and THF with Na/benzophenone ketyl; acetonitrile, dichloromethane and 1,2-dichloroethane with CaH_2), distilled under nitrogen and kept over 3 Å (for acetonitrile) or 4 Å molecular sieves. Silver molybdate (Ag_2MoO_4) was synthesised from silver nitrate (José M. Vaz Pereira) and sodium molybdate (Merck), and dried in vacuum at 60 °C for several hours prior to use. Bis(chloro)dioxomolybdenum, triphenylchlorosilane, 2,2′-bis[(4*S*)-4-benzyl-2-oxazoline] and $(CD_3)_2CO$ were purchased from Aldrich and used as received. Purely siliceous MCM-41 was synthesised as described previously using $[CH_3(CH_2)_{13}N(CH_3)_3]Br$ as the templating agent [28]. The surfactant was removed from the as-synthesised material by calcination at 540 °C for 6 h under air. Powder XRD (2θ (°), *hkl* in parentheses): 2.51 (1 0 0), 4.33 (1 1 0), 4.97 (2 0 0), 6.58 (2 1 0); $a = 2d_{1\,0\,0}/\sqrt{3} = 40.6$ Å. Prior to the grafting experiment, physisorbed water was removed from calcined MCM-41 by heating at 180 °C under reduced pressure for 2 h. ^{29}Si MAS NMR: δ = −100.4 ppm (Q^3), −108.8 ppm (Q^4). ^{29}Si CP MAS NMR: δ = −100.4 ppm (Q^3), −108.8 ppm (Q^4).

2.2. $[MoO_2Cl_2\{2,2'\text{-bis}[(4S)\text{-4-benzyl-2-oxazoline}]\}]$ (1)

The solvent adduct $MoO_2Cl_2(THF)_2$ was prepared by dissolving MoO_2Cl_2 (0.22 g, 1.1 mmol) in THF (20 mL) at 50 °C. 2,2′-Bis[(4*S*)-4-benzyl-2-oxazoline] (0.35 g, 1.1 mmol) was then added under nitrogen and the reaction mixture was left to stir at room temperature and protected from light for 2 h. The solution was evaporated to dryness and the resultant solid washed with *n*-hexane and diethyl ether, and finally dried under vacuum. Compound **1** was obtained as a white solid in 92% yield (0.52 g). Anal. found: C, 45.85; H, 4.12; N, 4.98. $C_{20}H_{20}N_2Cl_2MoO_4$ (519.23) requires C, 46.26; H, 3.88; N, 5.40. Selected IR (KBr, cm^{-1}): 3402br, 3058m, 3031m, 2950m, 1752w, 1650vs, 1603m, 1583w, 1498vs, 1454m, 1363m, 1327m, 1293m, 1261m, 1230vs, 1184m, 1159w, 1093w, 1029m, 998w, 943vs, 934s, 911vs, 885m, 858m, 754m, 711s, 610m, 579m, 496w, 382m, 348s, 277w, 243w, 213w, 206w. ^1H NMR [300 MHz, $(CD_3)_2CO$, 20 °C]: δ = 7.46–7.21 (m, 10H, Ph), 4.60–4.09 (m, 2H), 3.78–3.60 (m, 4H), 3.21–2.96 (m, 4H).

2.3. $[MoO_2(OSiPh_3)_2\{2,2'$-bis[(4S)-4-benzyl-2-oxazoline]$\}]$ (2)

A suspension of Ag_2MoO_4 (0.20 g, 0.50 mmol) in 1,2-dichloroethane (35 mL) and CH_3CN (3 mL) was stirred for 15 min. Ph_3SiCl (0.30 g, 1.00 mmol) was then added and the mixture was refluxed under nitrogen for 20 h. 2,2′-Bis[(4*S*)-4-benzyl-2-oxazoline] (0.16 g, 0.50 mmol) was added and the mixture stirred for a further 5 h at room temperature. The solution was filtered, evaporated to dryness, and the resultant product washed with *n*-hexane, diethyl ether and dried under vacuum. Compound **2** was obtained as a pale green solid in 80% yield (0.40 g). Anal. found: C, 67.42; H, 5.18; N, 2.95. $C_{56}H_{50}N_2MoO_6Si_2$ (999.12) requires C, 67.32; H, 5.04; N, 2.80. Selected IR (KBr, cm^{-1}): 3285s, 3061m, 3028m, 2929m, 1757w, 1684sh, 1654vs, 1521m, 1497m, 1454m, 1383m, 1205m, 1186m, 1039sh, 1029m, 954s, 912s, 800m, 748m, 742m, 699s, 509m, 350m. ^{1}H NMR [300 MHz, $(CD_3)_2CO$, 20 °C]: δ = 7.80–7.06 (m, 40H, Ph), 4.40–4.02 (m, 2H), 3.99–3.93 (m, 2H), 3.48–3.45 (m, 2H), 2.93–2.71 (m, 4H).

2.4. MCM-41 grafted with compound 1 (3)

A solution of $[MoO_2Cl_2\{2,2'$-bis[(4*S*)-4-benzyl-2-oxazoline]$\}]$ (**1**) (0.10 g, 0.19 mmol) in CH_2Cl_2 (30 mL) was added to a suspension of MCM-41 (0.75 g) in CH_2Cl_2 (20 mL), and the mixture was refluxed overnight under nitrogen. A pale green solid was recovered by filtration, washed with CH_2Cl_2 (3× 15 mL) and dried under reduced pressure for 3 h. Anal. found: C, 6.22; H, 1.35; N, 0.68; Cl, 0.7; Mo, 1.84. Selected IR (KBr, cm^{-1}): 3450s, 2984sh, 1761w, 1636m, 1517w, 1456w, 1383w, 1235vs, 1085vs, 964s, 908sh, 878sh, 797m, 744w, 700w, 668w, 575w, 456m. ^{29}Si MAS NMR: δ = −108.5 ppm (Q^4). ^{29}Si CP MAS NMR: δ = −101.4 ppm (Q^3), −109.2 ppm (Q^4).

2.5. Catalytic reactions

The catalytic oxidation of cyclooctene and *trans*-β-methylstyrene was carried out at either 40 °C (when dichloromethane was used as a co-solvent) or 55 °C (for all other systems) under air in a reaction vessel equipped with a magnetic stirrer. The vessel was loaded with olefin (1.7 mmol), catalyst (1% molar ratio of unsupported complex/substrate or 44 mg of **3**), oxidant (2.7 mmol *t*BuOOH, 5.5 M in decane) and, when used, 2 mL co-solvent. The course of the reaction was monitored using a gas chromatograph (Varian 3900) equipped with a capillary column (SPB-5, 20 m × 0.25 mm for cyclooctene, and CyclosilB 30 m × 0.25 mm for *trans*-β-methylstyrene) and a flame ionisation detector. The products were identified by GC–MS (HP 5890 Series II GC; HP 5970 Series Mass Selective Detector).

3. Results and discussion

3.1. Synthesis and characterisation

The chiral monomeric complex $[MoO_2Cl_2\{2,2'$-bis[(4*S*)-4-benzyl-2-oxazoline]$\}]$ (**1**) was obtained by simple ligand exchange with the solvent adduct $MoO_2Cl_2(THF)_2$ at room temperature (Plate 1). Attempts to prepare the corresponding organomolybdenum(VI) derivative $[MoO_2(CH_3)_2\{2,2'$-bis[(4*S*)-4-benzyl-2-oxazoline]$\}]$ by the treatment of compound **1** (prepared in situ or previously isolated) with the Grignard reagent CH_3MgCl were unsuccessful. The triphenylsiloxy compound $[MoO_2(OSiPh_3)_2\{2,2'$-bis[(4*S*)-4-benzyl-2-oxazoline]$\}]$ (**2**) was prepared by the reaction of silver molybdate with 2 equiv. of Ph_3SiCl and 1 equiv. of the chiral oxazoline N,N-ligand (Plate 1). Compounds **1** and **2** are soluble in chlorinated solvents and acetone, and either insoluble (**1**) or only sparingly soluble (**2**) in *n*-hexane. They are not stable at room temperature for long periods and decompose after prolonged exposure to air.

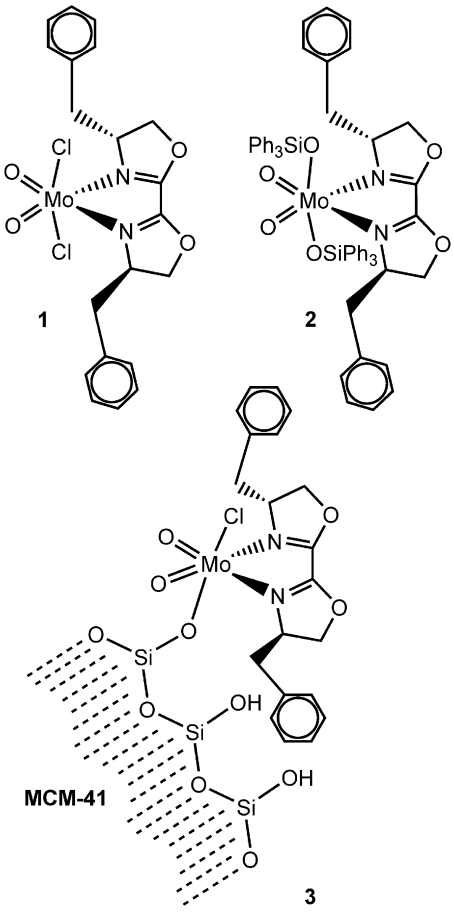

Plate 1.

The IR spectra of all of the complexes and of the starting materials were analysed and it was observed that the bis(oxazoline) spectrum exhibits significant changes upon complexation. Molybdenum(VI) complexes with the *cis*-dioxo unit typically show two very strong IR bands in the range 905–940 cm^{-1} [11], assigned to the Mo=O stretching modes, ν(Mo=O). For complex **1**, the symmetric and asymmetric stretching vibrations are observed at 943 and 911 cm^{-1}, respectively, in agreement with other complexes of this type containing 1,4-diazabutadiene [29], oxazoline [10] and other bidentate nitrogen ligands [30–33]. For the immobilised complex (**3**), although the spectrum is largely dominated by the MCM-41 contribution, the strong

bands corresponding to the ν(Mo=O) modes are visible at 964 and 908 cm^{-1}. Concerning complex **2**, the ν(Mo=O) modes are shifted to higher frequencies (954 and 912 cm^{-1}) as compared with complex **1**, indicating a strengthening of the Mo=O bonds when the Mo–Cl bonds are replaced by Mo–$OSiPh_3$ bonds. These values are also higher than those reported for similar complexes containing other bidentate nitrogen ligands, such as 2,2′-bipyridine (933 and 908 cm^{-1}) [34], phenanthroline, tetramethyl-phenanthroline and dimethyl-bipyridine (in the range of 912–897 cm^{-1}) [35].

Treatment of calcined and dehydrated MCM-41 with a refluxing dichloromethane solution of **1** gave a derivatised material (**3**) with a metal loading of 1.8 wt.% and a chlorine content of 0.7 wt.%. Microanalysis for C and N indicated that the oxazoline ligand content was about 0.24 mmol g^{-1}, which is in reasonable agreement with the expected value of 0.2 mmol g^{-1} based on the metal content. Powder XRD (not shown) and nitrogen adsorption studies at −196 °C confirmed that the structural integrity of the hexagonally ordered support was retained throughout the grafting process. The unmodified MCM-41 sample and the grafted material **3** exhibited reversible type IV isotherms (Fig. 1), characteristic of mesoporous solids (pore width between 2 and 50 nm, according to the IUPAC) [36]. For pristine MCM-41, a sharp capillary condensation/evaporation step appears in the relative pressure range of 0.25–0.4, reflecting the uniform pore size. A specific BET surface area of 1039 $m^2\ g^{-1}$ and a total pore volume (measured as the amount adsorbed at the relative pressure of 0.96) of 0.8 $cm^3\ g^{-1}$ were measured, which are in agreement with typical literature values [37]. Textural modifications were induced by the grafting treatment. The isotherm of the functionalised material reveals lower N_2 uptake, accounting for 16 and 27% decreases in specific BET surface area and total pore volume, respectively. The immobilisation of the complexes on the internal silica surface was also indicated by the decrease of the p/p_0 coordinate of the inflection point of the isotherm upon post-synthesis treatment [38]. The height of the capillary condensation step, which is related to the volume of pore space confined by adsorbate film on the pore walls, is much smaller in the case of compound **3**. Furthermore, the maximum of the pore size distribution curve determined by the BJH method decreased from 3.8 to 3.5 nm upon grafting of MCM-41 with compound **1**.

The chlorine content of 0.2 mmol g^{-1} in compound **3** suggests that each molybdenum species is grafted onto a surface silanol group with loss of one Cl ligand (Plate 1). Analogous monopodally anchored species of the type $MoO_2[(–O)_3SiO]Cl(THF)_n$ were previously characterised by EXAFS for MCM-41 grafted with the complex $MoO_2Cl_2(THF)_2$ [39]. The approximate abundance of surface silanol groups in calcined MCM-41 has been reported to be in the range of 1–3 nm^{-2} (1.5–5.0 mmol g^{-1} for a surface area of 1000 $m^2\ g^{-1}$), of which about 25% are free silanols (involving single and geminal groups) and the rest are hydrogen-bonded silanols [40,41]. Zhao et al. showed that only the free silanol groups on MCM-41 are readily accessible to silylating agents such as chlorotrimethylsilane [40]. We may assume therefore that complex **1** only interacts with free single silanol groups, resulting in the formation of Mo–O–Si linkages. The elemental analysis results indicate that at least 90% of the molybdenum species initially present in solution were successfully grafted onto the support.

The presence of molybdenum species monopodally anchored to the surface in material **3** was further evidenced by ^{29}Si MAS NMR spectroscopy (Fig. 2). The ^{29}Si MAS NMR spectrum of the unmodified MCM-41 support exhibits two broad overlapping peaks at $\delta = -100.4$ and −108.8 ppm assigned to, respectively, Q^3 and Q^4 units of the silica framework

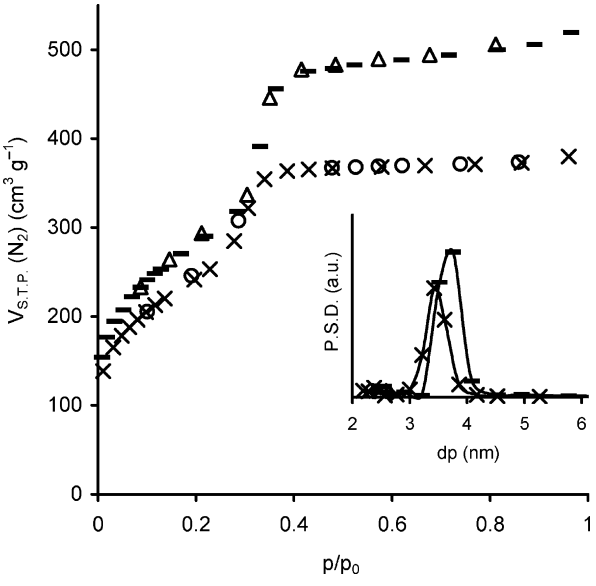

Fig. 1. Nitrogen adsorption [MCM-41 (−), **3** (×)] and desorption [MCM-41 (Δ), **3** (◯)] isotherms at −196 °C. The inset shows the pore size distribution (P.S.D.) curves of MCM-41 (−) and **3** (×).

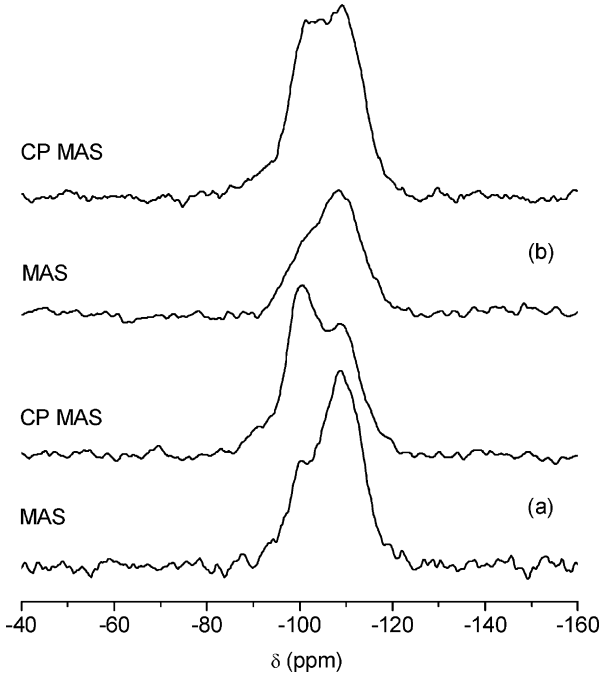

Fig. 2. ^{29}Si MAS and CP MAS NMR spectra of (a) unmodified MCM-41 and (b) MCM-41 grafted with compound **1** (**3**).

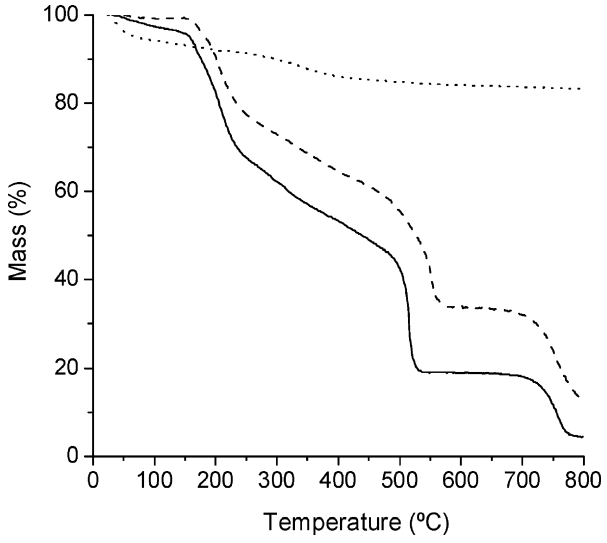

Fig. 3. TGA curves of $[MoO_2Cl_2\{2,2'\text{-bis}[(4S)\text{-4-benzyl-2-oxazoline}]\}]$ (**1**) (—), $[MoO_2(OSiPh_3)_2\{2,2'\text{-bis}[(4S)\text{-4-benzyl-2-oxazoline}]\}]$ (**2**) (– – –) and MCM-41 grafted with compound **1** (**3**) (· · ·).

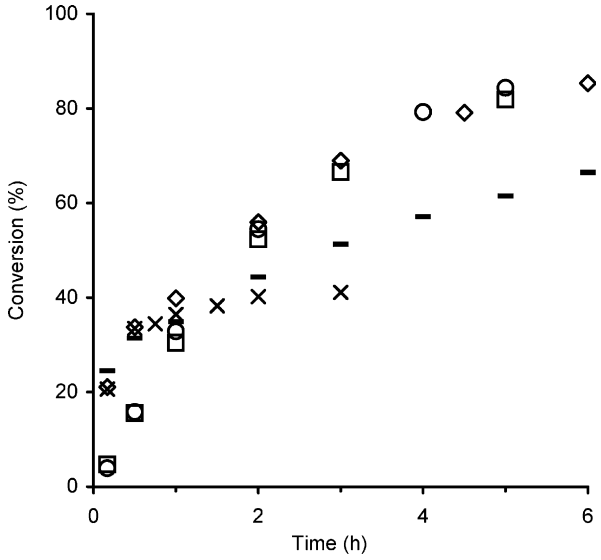

Fig. 4. Kinetic profiles of cyclooctene conversion at 55 °C in the presence of complex **1** (−) and the supported material **3** [run 1 (◊), run 2 (□), run 3 (○)], and for the leaching test of **3** (×).

$[Q^n = Si(OSi)_n(OH)_{4-n}]$. The ^{29}Si CP MAS NMR spectrum shows a marked increase in the relative intensity of the Q^3 resonance, confirming that these silicon atoms are attached to hydroxyl groups. A comparison of this spectrum with that for material **3** shows that upon grafting of MCM-41 with compound **1** the intensity of the Q^3 peak decreases relative to that for the Q^4 peak. This is consistent with the interaction of a significant number of single silanol groups with the immobilised molybdenum species, leading to the formation of Mo–O–Si linkages.

Fig. 3 shows the TGA curves for compounds **1**–**3** measured under air. The two complexes **1** and **2** exhibit similar traces containing three main decomposition steps up to 800 °C. The first step takes place between 150 and 250 °C (28.2% mass loss for **1**, 21.7% for **2**). This is followed by an extended mass loss of about 20% for both compounds up to 480 °C, and then abrupt losses of 27.1% for **1** up to 540 °C and 24.6% for **2** up to 580 °C. The final step for both compounds occurs between 690 and 800 °C, leaving residual masses of 4.3% for **1** and 12.4% for **2**. The derivatised material **3** exhibits a mass loss of 5.4% from room temperature up to 80 °C, attributed to the elimination of excess solvent in the channels and/or a small amount of water which had adsorbed when the sample was transferred to the TGA instrument. A further loss of 3.3% takes place up to 250 °C, followed by a more noticeable loss of 5.5% up to 410 °C. The combined mass loss of 8.8% for these two processes is in reasonable agreement with the value of 8.0% calculated for the complete removal of 0.25 mmol oxazoline ligand per gram of material. Unlike complex **1**, no further well-defined steps are evident up to 800 °C. Clearly, the thermal decomposition behaviour of complex **1** is significantly modified by the grafting reaction.

3.2. Catalysis

The catalytic performance of compounds **1** and **3** was first studied in the epoxidation of *cis*-cyclooctene, used as a model substrate, with *t*BuOOH as the oxygen donor, at 55 °C. The corresponding epoxide was the only observed product. The kinetic profiles are similar, suggesting that a similar reaction mechanism is involved (Fig. 4). For the epoxidation of olefins with *t*BuOOH in the presence of dioxomolybdenum(VI) complexes of the type $[MoO_2X_2L]$, a complex reaction mechanism has been proposed involving the coordination of the peroxide to the metal centre forming an oxidising species, followed by oxygen transfer to the olefin and production of *tert*-butanol as a by-product. The by-product may compete with *t*BuOOH for coordination to the metal centre, which, especially in the case of compound **1**, could explain why the reaction rate is higher at the beginning of the reaction [33,42,43]. The initial activity of **1** (147 mol mol_{Mo}^{-1} h^{-1}) is of the same order of magnitude as that reported previously for a dioxomolybdenum(VI) complex with a chiral pyridyl mentholate ligand, under similar reaction conditions (230 mol mol_{Mo}^{-1} h^{-1}) [11]. The initial specific activity of the MCM-41 grafted catalyst (**3**) (255 mol mol_{Mo}^{-1} h^{-1}) is higher than that for **1**, which may be due to the existence of a greater number of effective active species for the supported catalyst as compared with the bulk catalyst **1**, which is not completely soluble in the reaction medium (Table 1). On the other hand, and according to the above mechanistic assumptions, the formation of active oxidising species for olefin epoxidation may be faster when compound **1** is supported on MCM-41 due to the favourable adsorption of the polar oxidant molecules on the surface of the hydrophilic silica support.

The stability of the supported catalyst **3** was investigated by recycling the used catalyst twice after separating the solid from the reaction solution by centrifugation, washing thoroughly with *n*-hexane and drying at room temperature overnight. With the exception of the first hour of reaction, the kinetic curves of cyclooctene epoxidation are practically coincident for the three runs and epoxide selectivity was always 100% (Fig. 4). The initial activity decreased mainly from the first to the second run,

Table 1
Catalytic performance of compounds **1**–**3** for the epoxidation of cyclooctene (cyo) and *trans*-β-methylstyrene (mesty)

Cat./sub.	Solvent/oxidant[a]	Initial activity[b] (mol mol$_{Mo}^{-1}$ h^{-1})	Conversion[c] (%)	Selectivity[d] (%)	ee[e] (%) (10 min/24 h)
1/cyo	None/*t*BuOOH	147	100	100	–
3/cyo	None/*t*BuOOH	255 (run #1) 57 (run #2) 47 (run #3)	100 100 100	100	–
1/mesty	None/*t*BuOOH	15	64	100	<1
	DCE/*t*BuOOH	18	42	95	1/1
	Toluene/*t*BuOOH	7	23	94	<1/3[f]
	DCM/*t*BuOOH	8	24	100	2/<1
3/mesty	None/*t*BuOOH	47	56	100	<1
	DCE/*t*BuOOH	30	43	100	2/0
	Toluene/*t*BuOOH	31	23	100	13/0
	DCM/*t*BuOOH	0[g]	30	75	3/4
	None/cumeneOOH	218	67	25	<1
2/mesty	None/*t*BuOOH	34	76	65	<1

[a] DCE = 1,2-dichloroethane; DCM = dichloromethane; cumeneOOH = cumene hydroperoxide. Reactions were carried out at either 40 °C (with DCM) or 55 °C (for all other systems).
[b] Initial activity calculated after 10 min reaction.
[c] Conversion after 24 h.
[d] Selectivity towards total epoxides produced after 24 h. The corresponding diol was sometimes formed.
[e] (1*R*,2*R*)-Configuration, calculated at 10 min and 24 h reaction.
[f] (1*S*,2*S*)-Configuration.
[g] An induction period of ca. 20 min was observed.

which may be partly due to the presence of some (inactive) metal species formed during the first run by coordination of *t*BuOH. This decrease in initial activity could also be due to leaching of some active species under the applied oxidising conditions that were not removed by simple solvent extraction during catalyst preparation. Hence, the stability of **3** was further assessed by performing a leaching test. The reaction mixture was filtered after 30 min at the reaction temperature and the solution was left to react for a further 2.5 h (Fig. 4). The reaction continued in solution although to a much lower extent than that observed in the presence of the solid catalyst (within the following 2 h, conversion increased 8% compared to 16% when the solid catalyst was present). ICP-AES analysis indicated a 10% reduction in the original Mo loading. These results suggest that the reaction occurs to a certain extent in homogeneous phase.

The asymmetric catalytic performance of compounds **1**–**3** was investigated in the epoxidation of *trans*-β-methylstyrene at 55 °C, with *t*BuOOH as the oxidant and no additional solvent. As observed for cyclooctene, the kinetic profiles of *trans*-β-methylstyrene epoxidation in the presence of **1** or **3** are similar and the initial specific activity of compound **1** grafted onto MCM-41 (**3**) is higher than that of bulk **1** (Table 1). For **1** and **3**, the corresponding epoxide enantiomers, namely (1*R*,2*R*)-(+)-1-phenylpropylene oxide and (1*S*,2*S*)-(−)-1-phenylpropylene oxide, were the only observed reaction products, produced with relatively good yields (>55% at 24 h), albeit with negligible enantiomeric excess (ee < 0.1%, (1*R*,2*R*)-configuration), Table 1. The triphenylsiloxy compound **2** is somewhat more active (and less soluble) than the bis(chloro) complex **1** and yields ca. 50% of a racemic epoxide mixture after 24 h reaction, as well as the corresponding diols. As mentioned in Section 1, the results reported in the literature for the enantioselective epoxidation of unfunctionalised olefins with dioxomolybdenum(VI) complexes bearing oxazoline ligands, such as bidentate C_2-symmetric bis(oxazoline) [10] or phenolatooxazoline [14], using *t*BuOOH as oxidant, show very poor or no asymmetric induction. It was proposed that the absence of asymmetric induction could be due to the coordinative lability of the oxazoline ligands [10]. For methylenebis(oxazoline) complexes, the nature of the substituent at the C(4) position of the oxazoline ring had some effect on catalytic activity (phenyl giving better results than propyl and butyl, leading to 80% conversion of *trans*-β-methylstyrene after 4 h), but did not improve stereoselectivity [10].

There is evidence that the enantioselectivities of tungsten and molybdenum complexes can depend on the type of solvent [13]. We therefore studied the catalytic performance of compounds **1** and **3** in the epoxidation of *trans*-β-methylstyrene using either toluene or 1,2-dichloroethane (DCE) at 55 °C. For complex **1**, the highest initial activity was observed when the reaction was carried out with no additional solvent or with DCE (Table 1). The initial activity of **3** followed the order: no additional solvent > DCE ∼ toluene. The decrease in the initial activity of **3** when a co-solvent is used may be partly due to the decrease in the bulk density of the catalyst particles in the fluid media. After 24 h, conversion in each solvent is quite similar for compounds **1** and **3**. In the presence of compound **1**, minor amounts of the corresponding diol were formed when DCE or toluene were used, whereas with no co-solvent the epoxide selectivity was 100% at 64% conversion. For compound **3**, epoxide selectivity was 100% at 23–56% conversion, in any of these solvent systems. Unfortunately, the chiral induction abilities of **1** and **3**

were negligible for all solvents (Table 1). The most significant result was obtained for **3**/toluene, which initially gave 13% ee, with a preferential transfer of oxygen to the pro-*R* face of the olefinic bond, at 3% conversion, but eventually a racemic mixture was obtained at 23% conversion (24 h). It is possible that the epoxide coordinates reversibly to the metal centre and the catalyst catalyses racemisation during the reaction.

The catalytic performance of compounds **1** and **3** for the epoxidation of *trans*-β-methylstyrene was also tested using dichloromethane (DCM) as a co-solvent at 40 °C (Table 1). Whereas for complex **1** the epoxide selectivity was 100%, epoxide ring opening occurred for the derivatised material **3** at 24–30% conversion, and the ee was always very low. For example, compound **3** gave an ee [(1*R*,2*R*)-configuration] of 3–4% up to 30% conversion (24 h), and the corresponding diol was also formed with 25% selectivity.

A further experiment was carried out using cumene hydroperoxide as the oxidant instead of *t*BuOOH, since recent literature reports suggest that the former works well in enantioselective epoxidations [44]. With *trans*-β-methylstyrene as the substrate and compound **3** as catalyst, the initial activity increased remarkably from 47 to 218 mol mol_{Mo}^{-1} h^{-1} upon changing the oxidant (Table 1). However, the enantiomeric excess was negligible (as observed for *t*BuOOH under similar reaction conditions) and the corresponding diol was the main product with 75% selectivity.

4. Conclusions

Two novel dioxomolybdenum(VI) complexes of the type $[MoO_2X_2(N,N)]$ (X = Cl, $OSiPh_3$) containing a chiral bidentate oxazoline ligand have been prepared and characterised. Heterogenisation of the bis(chloro) complex in the ordered mesoporous silica MCM-41 by direct grafting gives mainly monopodally anchored species. The catalytic results show that the complex $[MoO_2Cl_2(N,N)]$ and the corresponding supported material are interesting catalysts for the liquid phase epoxidation of cyclooctene with *t*BuOOH, yielding 1,2-epoxycyclooctane quantitatively within 24 h at 55 °C. With *trans*-β-methylstyrene as the substrate, relatively high epoxide yields were obtained, but no catalytic asymmetric induction was observed. These results are comparable with previous studies of oxomolybdenum(VI) complexes bearing chiral oxazoline ligands, which generally revealed high catalytic activities but low enantiomeric excesses. The complex $[MoO_2(OSiPh_3)_2(N,N)]$ is somewhat more active than the bis(chloro) complex, producing a racemic mixture of epoxides plus the corresponding diols. Whereas the type of solvent and oxidant influences the catalytic activity of **1** and **3**, these reaction parameters do not have a significant effect on stereoselectivity.

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References

[1] P. Besgse, H. Veschambre, Tetrahedron 50 (1994) 8885.
[2] R.A. Sheldon, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, vol. 1, 2nd ed., Wiley–VCH, Weinheim, 2002, pp. 412–426.
[3] I. Ojima (Ed.), Catalytic Asymmetric Synthesis, VCH, Weinheim, 1993.
[4] M. Breuer, K. Ditrich, T. Habicher, B. Hauer, M. Keßeler, R. Stürmer, T. Zelinski, Angew. Chem. Int. Ed. 43 (2004) 788.
[5] F.E. Kühn, A.M. Santos, W.A. Herrmann, Dalton Trans. (2005) 2483.
[6] F.E. Kühn, J. Zhao, W.A. Herrmann, Tetrahedron: Asymmetry 16 (2005) 3469.
[7] S. Bellemin-Laponnaz, K.S. Coleman, J.A. Osborn, Polyhedron 18 (1999) 2533.
[8] S. Bellemin-Laponnaz, K.S. Coleman, P. Dierkes, J.-P. Masson, J.A. Osborn, Eur. J. Inorg. Chem. (2000) 1645.
[9] W.A. Herrmann, J.J. Haider, J. Fridgen, G.M. Lobmaier, M. Spiegler, J. Organomet. Chem. 603 (2000) 69.
[10] F.E. Kühn, A.M. Santos, A.D. Lopes, I.S. Gonçalves, J.E. Rodríguez-Borges, M. Pillinger, C.C. Romão, J. Organomet. Chem. 621 (2001) 207.
[11] A.A. Valente, I.S. Gonçalves, A.D. Lopes, J.E. Rodríguez-Borges, M. Pillinger, C.C. Romão, J. Rocha, X. García-Mera, New J. Chem. 25 (2001) 959.
[12] J. Fridgen, W.A. Herrmann, G. Eickerling, A.M. Santos, F.E. Kühn, J. Organomet. Chem. 689 (2004) 2752.
[13] X.-Y. Wang, H.-C. Shi, C. Sun, Z.-G. Zhang, Tetrahedron 60 (2004) 10993.
[14] M. Gómez, S. Jansat, G. Muller, G. Noguera, H. Teruel, V. Moliner, E. Cerrada, M. Hursthouse, Eur. J. Inorg. Chem. (2001) 1071.
[15] K. Kandasamy, H.B. Singh, R.J. Butcher, J.P. Jasinski, Inorg. Chem. 43 (2004) 5704.
[16] J. Zhao, X.G. Zhou, A.M. Santos, E. Herdtweck, C.C. Romão, F.E. Kühn, J. Chem. Soc., Dalton Trans. (2003) 3736.
[17] I.S. Gonçalves, A.M. Santos, C.C. Romão, A.D. Lopes, J.E. Rodríguez-Borges, M. Pillinger, P. Ferreira, J. Rocha, F.E. Kühn, J. Organomet. Chem. 626 (2001) 1.
[18] X. Zhou, J. Zhao, A.M. Santos, F.E. Kühn, Z. Naturforsch. B 59 (2004) 1223.
[19] S. Gago, J.E. Rodríguez-Borges, C. Teixeira, A.M. Santos, J. Zhao, M. Pillinger, C.D. Nunes, Z. Petrovski, T.M. Santos, F.E. Kühn, C.C. Romão, I.S. Gonçalves, J. Mol. Catal. A: Chem. 236 (2005) 1.
[20] A. Corma, A. Fuerte, M. Iglesias, F. Sánchez, J. Mol. Catal. A: Chem. 107 (1996) 225.
[21] A. Sakthivel, J. Zhao, G. Raudaschl-Sieber, M. Hanzlik, A.S.T. Chiang, F.E. Kühn, Appl. Catal. A: Gen. 281 (2005) 267.
[22] J.S. Johnson, D.A. Evans, Acc. Chem. Res. 33 (2000) 325.
[23] G. Helmchen, A. Pfaltz, Acc. Chem. Res. 33 (2000) 336.
[24] A. Pfaltz, Acta Chem. Scand. 50 (1996) 189.
[25] A. Pfaltz, Acc. Chem. Res. 26 (1993) 339.
[26] A.K. Ghosh, P. Mathivanan, J. Cappiello, Tetrahedron: Asymmetry 9 (1998) 1.
[27] J.A. Brito, M. Gómez, G. Muller, H. Teruel, J.-C. Clinet, E. Duñach, M.A. Maestro, Eur. J. Inorg. Chem. (2004) 4278.
[28] C.D. Nunes, A.A. Valente, M. Pillinger, A.C. Fernandes, C.C. Romão, J. Rocha, I.S. Gonçalves, J. Mater. Chem. 12 (2002) 1735.
[29] F.E. Kühn, A.M. Santos, A.D. Lopes, I.S. Gonçalves, E. Herdtweck, C.C. Romão, J. Mol. Catal. A: Chem. 164 (2000) 25.
[30] M. Groarke, I.S. Gonçalves, W.A. Herrmann, F.E. Kühn, J. Organomet. Chem. 649 (2002) 108.
[31] F.E. Kühn, E. Herdtweck, J.J. Haider, W.A. Herrmann, I.S. Gonçalves, A.D. Lopes, C.C. Romão, J. Organomet. Chem. 583 (1999) 3.
[32] F.E. Kühn, A.M. Santos, I.S. Gonçalves, C.C. Romão, A.D. Lopes, Appl. Organomet. Chem. 15 (2001) 43.

[33] F.E. Kühn, M. Groarke, E. Bencze, E. Herdtweck, A. Prazeres, A.M. Santos, M.J. Calhorda, C.C. Romão, I.S. Gonçalves, A.D. Lopes, M. Pillinger, Chem. Eur. J. 8 (2002) 2370.
[34] S.M. Bruno, B. Monteiro, M.S. Balula, C. Lourenço, A.A. Valente, M. Pillinger, P. Ribeiro-Claro, I.S. Gonçalves, Molecules 11 (2006) 298.
[35] A. Thapper, J.P. Donahue, K.B. Musgrave, M.W. Willer, E. Nordlander, B. Hedman, K.O. Hodgson, R.H. Holm, Inorg. Chem. 38 (1999) 4104.
[36] S.J. Gregg, K.S.W. Sing, Adsorption, Surface Area and Porosity, 2nd ed., Academic Press, London, 1982.
[37] (a) M.D. Alba, A. Becerro, J. Klinowski, J. Chem. Soc., Faraday Trans. 92 (1996) 849;
(b) A.A. Romero, M.D. Alba, W. Zhou, J. Klinowski, J. Phys. Chem. B 101 (1997) 5294.
[38] M. Kruk, M. Jaroniec, Langmuir 15 (1999) 5410.
[39] C.D. Nunes, A.A. Valente, M. Pillinger, J. Rocha, I.S. Gonçalves, Chem. Eur. J. 9 (2003) 4380.
[40] X.S. Zhao, G.Q. Lu, A.K. Whittaker, G.J. Miller, H.Y. Zhu, J. Phys. Chem. B 101 (1997) 6525.
[41] P.L. Llewellyn, F. Schüth, Y. Grillet, F. Rouquerol, J. Rouquerol, K.K. Unger, Langmuir 11 (1995) 574.
[42] A. Al-Ajlouni, A.A. Valente, C.D. Nunes, M. Pillinger, A.M. Santos, J. Zhao, C.C. Romão, I.S. Gonçalves, F.E. Kühn, Eur. J. Inorg. Chem. (2005) 1716.
[43] A.A. Valente, J. Morreira, A.D. Lopes, M. Pillinger, C.D. Nunes, C.C. Romão, F.E. Kühn, I.S. Gonçalves, New J. Chem. 28 (2004) 308.
[44] (a) W. Zhang, A. Basak, Y. Kosugi, Y. Hoshino, H. Yamamoto, Angew. Chem. Int. Ed. 44 (2005) 4389;
(b) A. Minatti, K.H. Dotz, Eur. J. Org. Chem. (2005) 268.