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Synthesis, characterization and catalytic studies of bis(chloro)dioxomolybdenum(VI)-chiral diimine complexes

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Abstract

Chiral 1,4-diazabutadienes (DAB) of the type R*–N=CPh–CPh=N–R* were prepared in quantitative yields by condensation of benzil with two equivalents of *R*-(+)-α-methylbenzylamine or *S*-(−)-α-methylbenzylamine, using $ZnCl_2$ as catalyst. The chiral diimine (1*R*,2*R*)-*N*,*N*′-dibenzylidenecyclohexane-1,2-diamine was also prepared by condensation of (1*R*,2*R*)-cyclohexane-1,2-diamine with two equivalents of benzaldehyde using a Dean–Stark adapter for the removal of water. Six-coordinate dioxomolybdenum(VI) complexes of the type $[MoO_2Cl_2L]$ containing the bidentate chiral ligands were prepared and characterized by FT-IR, FT Raman and NMR spectroscopy. The complexes were evaluated as catalysts for the asymmetric epoxidation of *cis*- and *trans*-β-methylstyrene by *tert*-butylhydroperoxide at either room temperature or 55 °C. The reactions proceeded with high retention of olefin configuration and high selectivity to the epoxide, but only for *cis*-β-methylstyrene were significant enantiomeric excesses (e.e.) obtained. With this substrate and the complex containing (1*R*,2*R*)-*N*,*N*′-dibenzylidenecyclohexane-1,2-diamine, (1*S*,2*R*)-*cis*-β-methylstyrene oxide was obtained in 77% e.e. at room temperature (24% conversion). Increasing the reaction temperature increased the epoxide yields but good enantiomeric excesses (≥65%) could only be achieved at low conversions (≤12%). The two complexes containing the chiral DAB ligands generally exhibited higher catalytic activity than the third complex but lower optical yields.

Keywords: Molybdenum; Oxide complexes; Chiral diimines; Homogeneous catalysis; Asymmetric epoxidation

1. Introduction

The enantioselective epoxidation of olefins is an important reaction in the synthesis of fine chemicals and pharmaceuticals [1]. Considerable progress has been made using transition metal catalysts bearing chiral ligands, although there is still much room for improvement [2,3]. While the Sharpless epoxidation using Ti–tartrate complexes is suitable for allylic alcohols [3,4], no such general solution exists for unfunctionalized olefins. Manganese salen and metalloporphyrin complexes show good selectivities with most *cis*-1,2-disubstituted olefins [3,5,6]. However, the selective epoxidation of *trans*-disubstituted alkenes is more difficult [7]. Two of the best reported enantiomeric excesses (e.e.) for the catalytic oxidation of *trans*-β-methylstyrene are 77% and 59% e.e. using chiral Cr-salen [8] and chiral *trans*-dioxoruthenium(VI) porphyrin [9] catalysts, respectively. These catalysts have a limitation, which is their modest catalytic activity, usually below 120 turnovers/h [10]. The practicality of the Cr-salen process is also restricted by the necessity of iodosylarenes as the stoichiometric oxidant.

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In the field of molybdenum(VI) chemistry, a broad variety of complexes are highly active catalysts for olefin epoxidation in the homogeneous phase. For example, molybdenum catalysts are commercially applied to the production of propylene oxide using *tert*-butyl hydroperoxide (TBHP) as the oxidant [11]. TBHP has a good thermal stability and is relatively easy to handle [11]. Furthermore, the by-product of the reaction, *tert*-butyl alcohol, is easy to separate by distillation and can be recycled or used for other industrial processes. Up until now the application of molybdenum(VI) catalysts in asymmetric olefin epoxidation has met with only limited success. Enantiomeric excesses of up to 53% are known with functionalized olefins as substrate, e.g. allylic alcohols or amides [12]. Unfortunately, in dioxomolybdenum(VI) complexes of the type [MoO_2(salen)] the Schiff base is forced to adopt a strained non-planar conformation due to the steric requirement of the *cis*-MoO_2 unit [13]. As a result the potential of such complexes as enantioselective catalysts is reduced and they can also have a low stability [14]. The same problems seem to hamper the successful application of Mo–porphyrin catalysts in asymmetric olefin epoxidation [15].

Bearing in mind the problems noted above for dioxomolybdenum(VI) complexes bearing tetradentate chiral ligands, research has focused instead on the synthesis of chiral monometallic complexes with the $[MoO_2]^{2+}$ core bearing bidentate or tridentate ligands derived from pyridyl alcohols [16–21], oxazolines and bis(oxazolines) [19,22,23], sugar derived Schiff bases [24], oximes, *cis*-diols and 8-phenylthiomenthols [25]. The enantiomeric excesses obtained for the epoxidation of unfunctionalized olefins using these complexes as catalysts are typically in the range 20–40%. We have been particularly interested in dioxomolybdenum(VI) complexes of the type [MoO_2X_2L] (X = Cl, Br, Me), which have proven to be versatile catalysts for olefin epoxidation with TBHP. Important properties, such as the solubility of the complex and the Lewis acidity of the metal centre, can be fine-tuned by variation of X and L. Some of the best catalysts are obtained with X = Cl and L = chelating diimine such as 1,4-diaza-1,3-butadiene [26–29]. This has led us to the preparation of [MoO_2Cl_2L] complexes bearing chiral diimines. In the present work, we describe three new complexes and their performance as enantioselective catalysts for the epoxidation of *cis*- and *trans*-β-methylstyrene using TBHP as the oxidant.

2. Experimental

2.1. Materials and methods

All preparations and manipulations were carried out using standard Schlenk techniques under nitrogen. Solvents were dried by standard procedures (THF over Na/benzophenone ketyl, CH_2Cl_2 over CaH_2), distilled under nitrogen and stored over 4 Å molecular sieves. Microanalyses were performed at the ITQB (by C. Almeida). IR spectra were obtained as KBr pellets using a FT-IR Mattson-7000 infrared spectrophotometer. Raman spectra were recorded on a Bruker RFS 100/S FT Raman spectrometer using a 1064 nm excitation of the Nd/YAG laser. ^{1}H and ^{13}C NMR spectra were obtained with Bruker CXP 300 and Bruker Avance DPX-400 spectrometers. Catalytic runs were monitored by chiral GC methods on a Hewlett-Packard (HP) 5890 Series II instrument equipped with a FID, a Supelco Alphadex 120 column and a HP 3396 Series II integration unit. MoO_2Cl_2 was obtained from Aldrich and used as received.

2.2. Preparation of chiral diimine ligands

2.2.1. Chiral 1,4-diaza-1,3-dienes

A mixture of benzil (2.1 g, 9.99 mmol) and (*R*)-(+)-α-methylbenzylamine or (*S*)-(−)-α-methylbenzylamine (3.09 g, 25.5 mmol) in THF (25 ml) was heated at 50 °C with stirring for 12 h under nitrogen in the presence of molecular sieves 3 Å (1.0 g) and zinc chloride (0.12 g, 0.9 mmol). The reaction mixture was cooled to room temperature, filtered and the remaining solids washed several times with THF (20 ml). The combined extracts were evaporated to dryness on a rotary evaporator and the resultant white solid purified by recrystallization from *n*-hexane.

*2.2.1.1. 1,4-Bis[(R)-1-phenylethyl]-2,3-diphenyl-1,4-diaza-1,3-butadiene (**1**).* Yield: 4.01 g (96%). Anal. found: C, 86.41; H, 6.68; N, 6.63; $C_{30}H_{28}N_2$ requires C, 86.50; H, 6.77; N, 6.72. $[\alpha]_D^{25}$ −60.1° (*c* 1, $CHCl_3$). FT-IR (KBr): ν_{max} (cm^{-1}) = 3081 (w), 3057 (w) (PhC–H st), 2982 (m), 2870 (m), 1661 (s) (C=N st), 1627 (s), 1592 (s) (Ph–C–C), 1577 (m), 1491 (s), 1449 (s), 1436 (m), 1365 (m), 1356 (m), 1314 (m), 1283 (m), 1274 (m), 1219 (s), 1173 (m), 1071 (m), 928 (s), 903 (m), 896 (m), 850 (s), 795 (s) (PhC–H), 782 (s), 775 (s), 765 (s), 726 (s), 712 (m), 699 (m), 637 (m), 615 (m), 555 (s), 521 (s), 484 (s). FT Raman: ν_{max} (cm^{-1}) = 3059 (s), 2983 (m), 2930 (m), 1661 (s), 1629 (s), 1597 (s), 1321 (m), 1220 (m), 999 (s), 784 (m), 638 (m). ^{1}H NMR (300 MHz, $CDCl_3$, TMS, r.t.): δ_H = 7.92–7.19 ppm (m, 20 H, Ph), 4.65 ppm (q, 2 H, *J* = 6.40 Hz, C*H*–CH_3), 1.53 ppm (d, 6 H, *J* = 6.40 Hz, CH–CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, TMS, r.t.): δ_C = 164.8 ppm (C=N), 144.9, 135.8, 135.2, 135.0, 131.2, 129.8, 129.5, 129.0, 128.8, 127.9, 127.3, 127.0 ppm (Ph), 62.6 ppm (C–N), 25.09 ppm (CH_3). m.p.:102–103 °C.

*2.2.1.2. 1,4-Bis[(S)-1-phenylethyl]-2,3-diphenyl-1,4-diaza-1,3-butadiene (**2**).* Yield: 3.99 g (96%). Anal. found: C, 86.38; H, 6.59; N, 6.54; $C_{30}H_{28}N_2$ requires C, 86.50; H, 6.77; N, 6.72. $[\alpha]_D^{25}$ +59.9° (*c* 1, $CHCl_3$). FTIR (KBr): ν_{max} (cm^{-1}) = 3081 (w), 3056 (w), 3026 (w) (PhC–H st), 2982 (m), 2928 (w), 2870 (m), 1661 (s) (C=N st), 1627 (s), 1592 (s) (Ph–C–C), 1577 (s), 1491 (s), 1449 (s), 1436 (m), 1365 (m), 1356 (m), 1314 (m), 1283 (m), 1275 (m), 1219 (s), 1173 (m), 1080 (m), 1071 (m), 928 (s), 903 (s), 896 (m), 850 (s), 795 (s) (PhC–H), 782 (m), 775 (s), 765

(s), 726 (s), 712 (m), 700 (m), 637 (s), 616 (m), 555 (s), 521 (s), 485 (s). FT Raman: ν_{max} (cm^{-1}) = 3059 (s), 2983 (m), 2930 (m), 1661 (s), 1629 (s), 1597 (s), 1321 (m), 1220 (m), 999 (s), 784 (m), 638 (m). ^1H NMR (300 MHz, $CDCl_3$, TMS, r.t.): δ_H = 7.92–7.19 ppm (m, 20 H, Ph), 4.65 ppm (q, 2 H, J = 6.40 Hz, C*H*–CH_3), 1.53 ppm (d, 6 H, J = 6.40 Hz, CH–C*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, TMS, r.t.): δ_C = 164.8 ppm (C=N), 144.9, 135.8, 135.2, 135.0, 131.2, 129.8, 129.5, 129.0, 128.8, 127.9, 127.3, 127.0 ppm (Ph), 62.6 ppm (CH–N), 25.09 ppm (CH_3). m.p.: 102–103 °C.

2.2.2. (1R,2R)-N,N′-dibenzylidenecyclohexane-1, 2-diamine (3)

Benzaldehyde (380 μl, 3.85 mmol, 2.1 equiv) was added to a solution of (1*R*,2*R*)-cyclohexane-1,2-diamine (209 mg, 1.83 mmol) in benzene (15 ml) and the reaction mixture was refluxed under nitrogen with a Dean–Stark adapter until all the water had been removed (approximately 4 h). The solution was evaporated to dryness and the resultant yellow powder dried under reduced pressure. Yield: 0.45 g (85%). Anal. found: C, 82.58; H, 7.47; N, 9.55; $C_{20}H_{22}N_2$ requires C, 82.72; H, 7.64; N, 9.65. FT-IR (KBr): ν_{max} (cm^{-1}) = 3078 (w), 3058 (w), 3042 (w), 3030 (w), 3017 (m) (PhC–H st), 2948 (m), 2926 (m), 2856 (m), 2846 (w) (cyclohexane C–H st), 1643 (vs) (C=N st), 1598 (w), 1578 (s), 1493 (m), 1449 (vs), 1375 (s), 1338 (m), 1287 (m), 1216 (m), 1165 (m), 1156 (m), 1086 (m), 1064 (s), 938 (m), 864 (s), 837 (s), 760 (s), 754 (s), 694 (vs), 500 (m), 489 (m), 429 (s). ^1H NMR (300 MHz, C_6D_6, TMS, r.t.): δ_H = 8.09 ppm (s, 2H), 7.65–7.62 ppm (m, 4H), 7.00–6.98 ppm (m, 6H), 3.51–3.41 ppm (m, 2H), 1.88–1.78 ppm (m, 6H), 1.49–1.45 ppm (m, 2H).

2.3. Preparation of chiral (dichloro)dioxomolybdenum(VI) complexes

2.3.1. Complexes bearing chiral 1,4-diaza-1,3-dienes

The solvent adduct [$MoO_2Cl_2(THF)_2$] was prepared by evaporating to dryness a solution of MoO_2Cl_2 (0.24 g, 1.2 mmol) in THF (5 ml). CH_2Cl_2 (5 ml) was added and the resulting colorless solution added dropwise to a solution of *R,R*-diimine (**1**) or *S,S*-diimine (**2**) (0.50 g, 1.2 mmol) in CH_2Cl_2 (10 ml). After stirring the mixture for 2 h at room temperature the solution was filtered and evaporated to dryness under reduced pressure. The yellow solid products were dried under vacuum for 1 h.

2.3.1.1. [MoO_2Cl_2\{1,4-bis[(R)-1-phenylethyl]-2,3-diphenyl-1,4-diaza-1,3-butadiene\}] (4).

Anal. found: C, 58.41; H, 4.43; N, 4.39; $C_{30}H_{28}Cl_2MoN_2O_2$ requires C, 58.55; H, 4.59; N, 4.55. FT-IR (KBr): ν_{max} (cm^{-1}) = 3060 (m), 2977 (m), 1671 (s) (C=N st), 1624 (s), 1591 (s), 1495 (m), 1449 (s), 1384 (m), 1316 (m), 1273 (m), 1212 (s), 1174 (s), 1084 (m), 1065 (m), 1029 (m), 998 (m), 952 (s) (ν_{sym} Mo=O), 912 (s) (ν_{asym} Mo=O), 873 (w), 764 (m), 697 (m), 643 (m), 522 (m), 473 (m), 386 (m), 324 (m). FT Raman: ν_{max} (cm^{-1}) = 3064 (s), 2984 (m), 2936 (m), 1679 (m), 1627 (m), 1593 (s), 1493 (m), 1451 (m), 1327 (m), 1289 (m), 1221 (m), 1165 (w), 1023 (m), 1000 (s), 953 (m), 916 (m), 797 (m), 390 (w), 310 (w), 250 (w), 174 (w). ^1H NMR (300 MHz, CD_2Cl_2, TMS, r.t.): δ_H = 8.26–7.29 ppm (m, 20H, Ph), 4.95 ppm (br, 2H), 1.93 ppm (d, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS, r.t.): δ_C = 134.9, 133.0, 130.0, 129.9, 129.8, 129.0, 128.9, 127.4 ppm (Ph), 62.8 ppm (C–N), 25.1 ppm (CH_3).

2.3.1.2. [MoO_2Cl_2\{1,4-bis[(S)-1-phenylethyl]-2,3-diphenyl-1,4-diaza-1,3-butadiene\}] (5).

Anal. found: C, 58.31; H, 4.33; N, 4.23; $C_{30}H_{28}Cl_2MoN_2O_2$ requires C, 58.55; H, 4.59; N, 4.55. FT-IR (KBr): ν_{max} (cm^{-1}) = 3056 (m), 2978 (m), 2924 (m), 1671 (s) (C=N st), 1625 (m), 1591 (m), 1579 (m), 1494 (m), 1449 (s), 1316 (m), 1286 (m), 1273 (m), 1224 (s), 1213 (s), 1174 (s), 1084 (m), 1065 (m), 998 (m), 952 (s) (ν_{sym} Mo=O), 911 (s) (ν_{asym} Mo=O), 872 (w), 764 (m), 698 (s), 682 (m), 643 (m), 624 (m), 613 (m), 523 (m), 387 (w), 324 (w). FT Raman: ν_{max} (cm^{-1}) = 3066 (s), 2985 (m), 2936 (m), 1678 (m), 1629 (m), 1594 (s), 1450 (m), 1287 (m), 1223 (m), 1162 (m), 1024 (m), 1001 (s), 952 (m), 883 (m), 788 (m), 616 (m), 311 (m), 253 (m). ^1H NMR (400 MHz, $CDCl_3$, TMS, r.t.): δ_H = 8.23–7.39 ppm (m, 20H, Ph), 4.91 ppm (m, 2H), 1.97 ppm (d, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS, r.t.): δ_C = 137.4, 134.8, 130.5, 130.0, 129.9, 129.3, 129.0, 127.5, 62.5 ppm (C–N), 25.5 ppm (CH_3).

2.3.2. [MoO_2Cl_2(1R,2R)-N,N′-dibenzylidenecyclohexane-1,2-diamine] (6)

The solvent adduct $MoO_2Cl_2(THF)_2$ was prepared by evaporating to dryness a solution of MoO_2Cl_2 (0.99 g, 0.5 mmol) in THF (5 ml). CH_2Cl_2 (4 ml) was added and the resulting colorless solution added dropwise to a solution of (1*R*,2*R*)-*N*,*N*′-dibenzylidenecyclohexane-1,2-diamine (**3**) (0.150 g, 0.5 mmol) in CH_2Cl_2 (5 ml). The reaction mixture changed color immediately to light brown. After stirring for 2 h at room temperature, the suspension was concentrated and hexane was added to precipitate the product, which was filtered and washed with diethyl ether. The resultant light brown solid was dried under vacuum. Anal. found: C, 48.90; H, 4.33; N, 5.60; $C_{20}H_{22}Cl_2MoN_2O_2$ requires C, 49.10; H, 4.53; N, 5.73. FT-IR (KBr): ν_{max} (cm^{-1}) = 3033 (w), 3003 (w), 2938 (m), 2864 (w), 1696 (m), 1665 (s) (C=N st), 1597 (s), 1440 (m), 1334 (m), 1310 (m), 1224 (m), 1204 (m), 1165 (m), 1142 (m), 1075 (m), 1056 (m), 1028 (m), 946 (s) (ν_{sym} Mo=O), 908 (s) (ν_{asym} Mo=O), 754 (s), 684 (s), 485 (w), 475 (w), 449 (w), 367 (w). ^1H NMR (400 MHz, $CDCl_3$, TMS, r.t.): δ_H = 9.00 ppm (s, 2H), 8.36–7.49 ppm (m, 10H), 5.27–5.02 ppm (m, 2H), 2.24–1.95 ppm (m, 6H), 1.60–1.57 ppm (m, 2H).

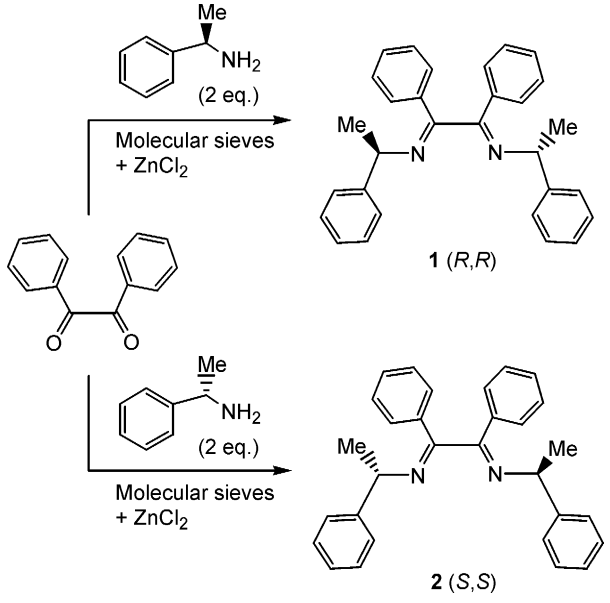
2.4. Catalytic epoxidation reactions with compounds 4–6

Cis- or *trans*-β-methylstyrene (200 mg, 1.7 mmol), mesitylene as internal standard (100 mg) and 1.0 mol% **4**–**6** as catalyst (17 μmol) were dissolved in dry toluene (2 ml). After addition of *tert*-butylhydroperoxide solution (615 μl 5.5 M in decane) the reaction mixture was stirred for up to 24 h at either room temperature or 55 °C. The course of each reaction was monitored by quantitative GC-analysis. Samples were taken every thirty minutes, diluted with chloroform, and chilled in an ice bath. Manganese sulfate and a catalytic amount of manganese dioxide were added for the removal of water and destruction of hydroperoxide, respectively. After the gas evolution ceased the slurry was filtered over a filter-equipped Pasteur pipette and the filtrate injected into the GC column. The enantiomeric excesses and conversions were determined by chiral GC methods. The conversion was determined by a calibration curve ($r^2 = 0.999$) recorded prior to the reaction course.

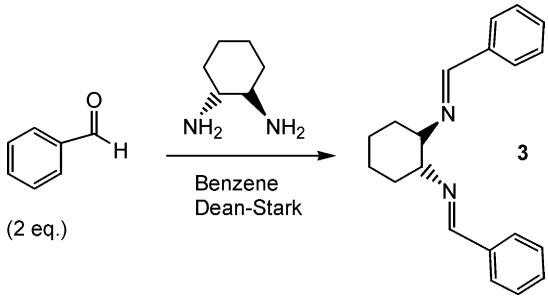
3. Results and discussion

3.1. Synthesis and characterization

The chiral 1,4-diaza-1,3-butadienes R*–N=CPh–CPh=N–R* [(*R*,*R*)-diimine (**1**) and (*S*,*S*)-diimine (**2**)] were prepared in very good yields by condensation of benzil with two equivalents of *R*-(+)-α-methylbenzylamine or *S*-(−)-α-methylbenzylamine, respectively, using $ZnCl_2$ as catalyst (Scheme 1). A nonpolar solvent was used to avoid the competing addition reaction and 3 Å molecular sieves were added as drying agent. The chiral diimine (1*R*,2*R*)-*N*,*N*′-dibenzylidenecyclohexane-1,2-diamine (**3**) was prepared by condensation of (1*R*,2*R*)-cyclohexane-1,2-diamine with two equivalents of benzaldehyde using a Dean–Stark adapter for the removal of water (Scheme 2). The identity and purity of the ligands **1**–**3** were confirmed by spectroscopic characterization and elemental analysis (see Section 2 for full details).



Scheme 1.



Scheme 2.

The chiral dioxomolybdenum(VI)-diimine complexes with the general formula $[MoO_2Cl_2L^*]$ (**4**–**6**, Plate 1) were obtained by simple ligand exchange with the solvent adduct $[MoO_2Cl_2(THF)_2]$ at room temperature. This is a convenient route to distorted octahedral dioxomolybdenum(VI) complexes bearing bidentate Lewis base ligands [26–29]. The complexes **4** and **5** are soluble in dichloromethane and can only be purified by washing with *n*-hexane. They are not

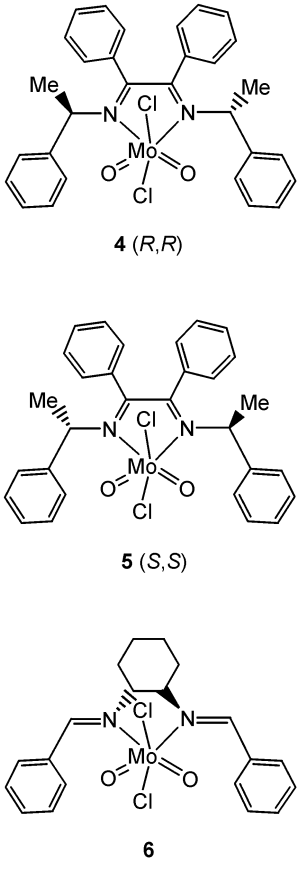


Plate 1.

stable at room temperature for long periods and decompose quickly in the presence of air. Compound **6** is more stable and does not decompose at room temperature, in the solid state, even after several weeks and can be handled in air for brief periods of time. It is very soluble in polar solvents such as $CHCl_3$ and CH_2Cl_2, and is completely insoluble in nonpolar solvents such as *n*-hexane and diethyl ether. The complexes **4**–**6** were characterized by elemental analysis and spectroscopic techniques. In particular, the ^1H NMR spectra are straightforward and in accord with species containing a κ^2-bonded diimine ligand. The existence of a two-fold axis in the molecules for **4** and **5** is indicated by the presence of only one set of signals for the phenyl substituents at the diazabutadiene chelate ring. The complexes **4**–**6** display their symmetric and asymmetric IR stretching vibrations for the *cis*-dioxo unit at about 950 and 910 cm^{-1}, respectively, in agreement with other complexes of this type [26–29].

3.2. Catalytic results

Complexes **4**–**6** were evaluated as catalysts for the asymmetric epoxidation of *cis*- and *trans*-β-methylstyrene using *tert*-butylhydroperoxide (TBHP) as oxidant and toluene as solvent at either room temperature or 55 °C. A substrate:oxidant:catalyst ratio of 100:200:1 was used. Catalytic runs are shown in Fig. 1 and the enantiomeric excesses obtained are summarized in Table 1. The overall yields are shown in Fig. 2. For the three complexes studied, the reactions proceeded with high retention of olefin configuration and high selectivity to the epoxide, but only for *cis*-β-methylstyrene were significant enantiomeric excesses obtained. During the first few hours of reaction at 55 °C the epoxide yields for *cis*- and *trans*-β-methylstyrene followed the trends **4** ∼ **5** > **6** and **4** ∼ **5** ≫ **6**, respectively (Fig. 1). At a given point the yields in the presence of **6** were roughly equal for both substrates, while for **4** and **5** the conversion of *trans*-β-methylstyrene was significantly higher than that for *cis*-β-methylstyrene. However, after 24 h the yields in the presence of **4** and **5** tended to equalize (Fig. 2). Compound **6** exhibits the highest enantioselectivities for both substrates (Table 1), but unfortunately also the lowest epoxide yields. Nevertheless, the complex seems to be stable under the applied reaction conditions since conversion increases steadily with time, reaching values of 65% for the *trans* isomer and 45% for the *cis* isomer after 24 h at 55 °C. The downside is that enantioselectivities decrease as the reactions progress. For example, in the presence of **6** at 55 °C, (1*S*,2*R*)-*cis*-β-methylstyrene oxide was formed in 65% e.e. at 12% conversion (4 h), decreasing to 22% e.e. at 45% conversion (24 h). The situation improved at room temperature at the expense of catalytic activity. Thus, in the presence of **6** at r.t., the (1*S*,2*R*)-epoxide was formed in 85% e.e. at 7% conversion of *cis*-β-methylstyrene (4 h), decreasing to 77% e.e. at 24% conversion (24 h).

Table 1
Enantiomeric excesses obtained in asymmetric epoxidation with TBHP and compounds **4**–**6** after 4 h

	Trans-β-methylstyrene		*Cis*-β-methylstyrene	
	r.t.	55 °C	r.t.	55 °C
4	2*R*,*R*	1*R*,*R*	32*S*,*R*	32*S*,*R*
5	–	1*S*,*S*	33*S*,*R*	24*S*,*R*
6	12*R*,*R*	10*R*,*R*	85*S*,*R*	65*S*,*R*

The particular behavior of complex **6** (higher enantioselectivity/lower activity) is not surprising when we consider the molecular structure. Hence, on the one hand the chiral ligand remains chelated to the Mo^{VI} center during the reaction

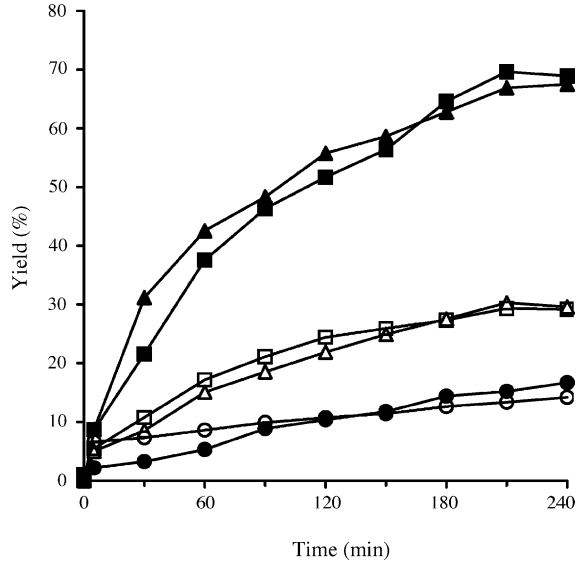


Fig. 1. Catalytic activity of compounds **4**–**6** for the epoxidation of *cis*-β-methylstyrene [**4** (△), **5** (□), **6** (○)] and *trans*-β-methylstyrene [**4** (▲), **5** (■), **6** (●)] with TBHP at 55 °C.

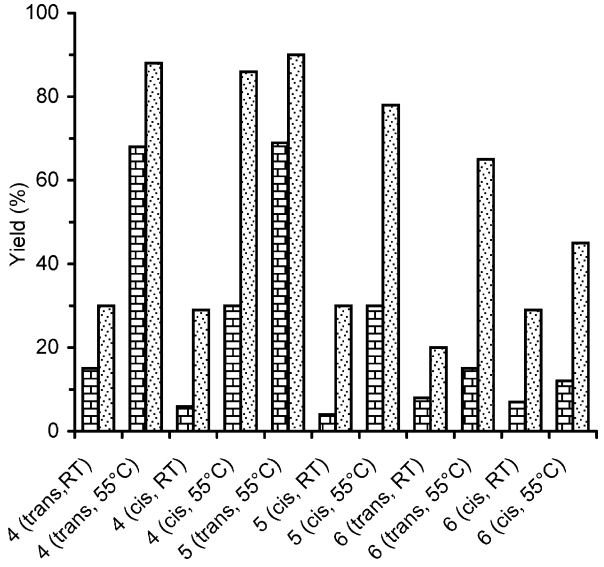


Fig. 2. Epoxide yields obtained after 4 (bricks) and 24 h (dots) for the reaction of *cis*-β-methylstyrene and *trans*-β-methylstyrene with TBHP in the presence of compounds **4**–**6** at either room temperature or 55 °C.

but on the other hand it is the most sterically hampered for the approach of the substrate. The presence of the bulky equatorial groups and the use of an unhindered diamine precursor improves the selectivity by hindering all side-on olefin approaches with the exception of an approach to the cyclohexane ring, as previously observed by Jacobsen et al. with salen systems bearing different substituents [5b,c]. Compounds **4** and **5** may undergo opening of the chelating ring contributing to a faster reaction but to a loss of enantioselectivity. Such opening may be accelerated by the accumulation of the by-product *t*-BuOH in the reaction mixture. A lowering of the enantioselectivity with increasing conversion was described by Herrmann et al. in the epoxidation of *cis*-β-methylstyrene catalyzed by a chiral 2′-pyridyl alcoholate derived from fenchone, $MoO_2(fenpy)_2$ [18]. The loss of selectivity along the reaction evolution was attributed to opening of the chelate ring by protonation of the Mo–O bond of one fenpy ligand.

4. Concluding remarks

Three novel dioxomolybdenum(VI) complexes bearing chiral diimine ligands have been prepared and characterized. The catalytic results indicate that these types of complexes are potentially interesting for the enantioselective epoxidation of *cis*-1,2-disubstituted olefins using TBHP as the mono-oxygen source. Further research to identify more effective catalysts within the group of $[MoO_2Cl_2L^*]$ complexes is required and is currently under way in our laboratories.

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