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A novel and efficient catalytic epoxidation of olefins with adducts derived from methyltrioxorhenium and chiral aliphatic amines

Stefano Vezzosi [a], Anna Guimerais Ferré [a,1], Marcello Crucianelli [a,*], Claudia Crestini [b], Raffaele Saladino [c,*]

[a] Dipartimento di Chimica, Ingegneria Chimica e Materiali, Università dell'Aquila, via Vetoio, 67010, Coppito (AQ), Italy
[b] Dipartimento di Scienze e Tecnologie Chimiche, Università di Tor Vergata, via della Ricerca Scientifica, 00133 Roma, Italy
[c] Dipartimento di Agrobiologia e Agrochimica, Università della Tuscia, via S. Camillo de Lellis, 01100 Viterbo, Italy

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ABSTRACT

Nitrogen-based adducts derived from methyltrioxorhenium(VII) and chiral aliphatic amines have been synthesized and applied to the efficient catalytic epoxidation of olefins with urea hydrogen peroxide complex as the primary oxidant. These complexes retain their catalytic activity when microencapsulated in polystyrene. A moderate steroinduction was obtained in the epoxidation of prochiral olefins with complexes between methyltrioxorhenium and chiral *trans*-1,2-cyclohexyldiamine. The values of steroinduction were found to increase after the microencapsulation process.

1. Introduction

Methyltrioxorhenium(VII) (CH_3ReO_3, MTO) [1] is one of the most active catalysts for the activation of hydrogen peroxide (H_2O_2). The active catalytic forms are a monoperoxo metal [$MeRe(O)_2(O_2)$] and a bisperoxo metal [$MeRe(O)(O_2)_2$] complexes and/or their adducts with solvent molecules [2]. Among the synthetic applications of MTO, the epoxidation of olefins is receiving increased attention. The most relevant drawback of this reaction is the concomitant ring-opening of the newly formed oxiranyl ring to diols due to the acidic properties of rhenium compounds. To date, the procedures developed to avoid this side reaction require the use of an anhydrous reaction medium and urea hydrogen peroxide adduct (UHP) as the primary oxidant. Low-molecular-weight compounds bearing one or more nitrogen atoms also have been used as mediators for oxidation. In this latter case, adducts of MTO with Lewis bases, of general formula MTO/L_n [where L = ligand, $n = 1$ (monodentate) or 2 (bidentate)], have been prepared by reaction with aromatic amines, such as pyridine, pyridine derivatives, quinuclidine, anilines, toluidines, pyrazoles, and others [1b]. These adducts inhibit the formation of diols by tuning the electronic properties of MTO. MTO/L_n adducts exist in a fluxional equilibrium, and their stability depends on the physical and chemical properties of the ligand and of the reaction medium. Recently, heterogeneous rhenium catalysts based on microencapsulation of MTO-derived adducts on polystyrene (2% cross-linked with divinylbenzene) were prepared. These compounds are efficient and selective catalysts in wide variety of oxidative reactions, maintaining their stability for successive recycling experiments [3,4]. Of note, the reactivity and selectivity of MTO/L_n adducts inside the microcapsule can be modified with respect to homogeneous conditions due to the effect of the polymeric matrix on the stability of the complex.

Despite the large number of MTO/L_n adducts described in the literature, only a few examples of complexes with aliphatic amines have been reported, probably because of their low stability [5]. On the other hand, the preparation of adducts between MTO and aliphatic amines is highly desirable, as in, for example, the synthesis of chiral rhenium complexes useful for stereoselective oxidations. To date, this represents one of the most stimulating challenges in MTO chemistry [1c]. With the aim of evaluating this topic in depth, herein we report the synthesis of homogeneous and heterogeneous rhenium catalysts based on the formation of stable adducts between MTO and chiral aliphatic amines. The properties of the aliphatic amine necessary for the formation of isolable MTO adducts were defined by comparing different monodentate and bidentate amines as ligands for the rhenium atom. Data on the efficient oxidation of some representative prochiral olefins affording sensitive epoxides also are reported.

* Corresponding authors. Faxes: +39 0 862 433753; +39 0 761 357242.
E-mail addresses: marcello.crucianelli@univaq.it (M. Crucianelli), saladino@unitus.it (R. Saladino).

[1] On leave from Department of Organic Chemistry, University of Barcelona, Martí i Franqués 1, 08028 Barcelona, Catalonia, Spain.

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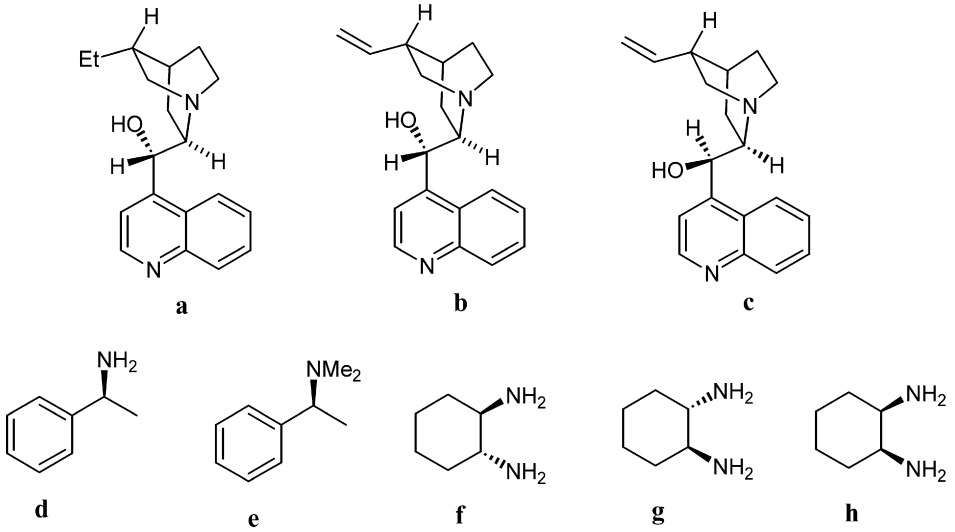
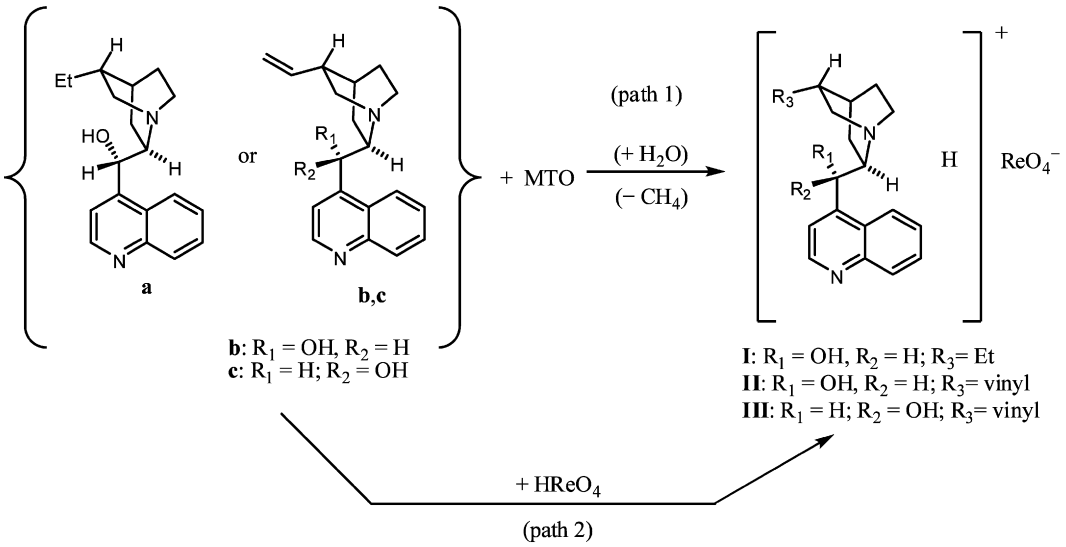


Fig. 1. Structures of chiral amines **a**–**h**.



Scheme 1. Formation of perrhenate salts **I**–**III** from reaction of MTO (or perrhenic acid) with chiral amines **a**–**c**.

2. Experimental

All commercial products were purchased in the highest purity grade available and were used as such. Methyltrioxorhenium(VII), hydrogen peroxide (35% aqueous solution), aliphatic amines (**a**–**h**), olefins **1**–**4**, and perrhenic acid were purchased from a commercial source (Aldrich). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker (AC-200 MHz) instrument. Attenuated total reflection infrared (ATR-IR) spectroscopic analyses were performed, at room temperature, with a Perkin–Elmer Spectrum One spectrometer equipped with an ATR-IR cell. IR spectra were recorded by averaging 32 scans, with a resolution of 4 cm^{-1}. Gas chromatography-mass spectrometry (GC-MS) analyses of the reaction products were performed using a Varian 2000 GC-MAS instrument, with a 30 m × 0.32 mm × 0.25 μm film thickness (cross-linked 5% phenylmethylsiloxane) column and chromatography-grade helium as the carrier gas. Yields and conversions of the reactions were quantified using *n*-octane as internal standard. In GC calculations, all peaks amounting to at least 0.5% of the total products were taken into account. Enantiomeric excess (ee) was evaluated using a Hewlett–Packard 6890 series gas chromatograph equipped with a flame ionization detector, using 30 m × 0.25 mm × 0.25 μm film thickness BETA-DEX-325 fused silica capillary column. When necessary, ^{1}H and ^{13}C-NMR analyses of products were performed after flash-chromatographic purification on columns packed with silica gel (230–400 mesh), and compared with authenticated samples. Mass spectra were recorded with an electron beam of 70 eV. For the scanning electron microscopy (SEM) photographs, samples were spitter-coated with gold (20 nm). Elemental analyses (C, H, N) were performed with a Fisons Instruments 1108 CHNS-O elemental analyzer.

2.1. General procedure for the preparation of perrhenate salts **I**–**V**

To a methanol (1.0 mL) solution containing 0.1 mmol of appropriate amine (**a**–**e**, Fig. 1), 0.1 mmol of perrhenic acid were added under stirring, and the reaction was maintained at room temperature for 1 h. After evaporation of the solvent, the residue was dried under high vacuum, affording a quantitative yield of the corresponding perrhenate salt (Schemes 1–3) as a white powder.

2.1.1. Hydrocinchonine perrhenate salt (**I**)

IR (KBr disc) (cm^{-1}) 3300, 2940, 1500, 1450, 890, 870. ^{1}H NMR (CD_3OD) δ 8.85–8.75 (m, 1H), 8.10–7.95 (m, 2H), 7.80–7.60 (m, 3H), 5.93 (s, 1H), 3.95–3.82 (m, 1H), 3.65–3.15 (m, 4H), 2.35–2.20 (m,

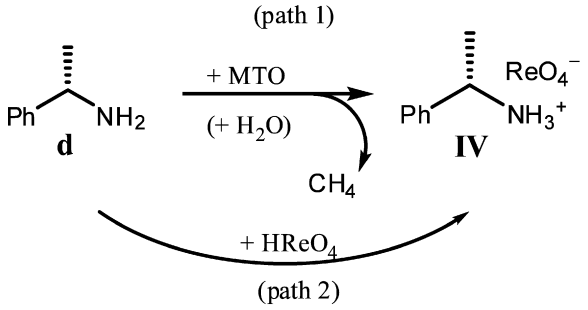
1H), 1.90–1.68 (m, 4H), 1.60–1.40 (m, 2H), 1.15–1.00 (m, 1H), 0.85 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (CD_3OD) δ 151.02; 148.72; 148.16; 131.16; 130.27; 129.02; 126.31; 123.67; 120.27; 68.94; 61.69; 52.05; 50.79; 36.16; 26.28; 25.32; 24.52; 19.04; 11.74.

2.1.2. Cinchonine perrhenate salt (**II**)

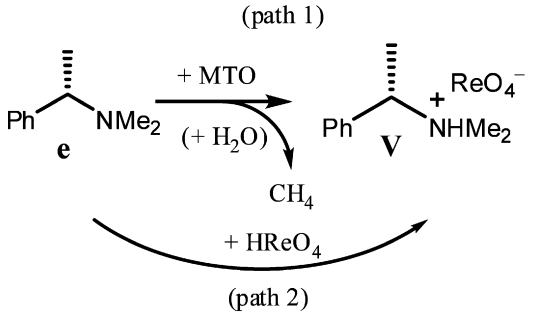
IR (KBr disc) (cm^{-1}) 3300, 2940, 1500, 890, 860. ^{1}H-NMR (CD_3OD) δ 8.82 (br. s, 1H), 8.15–7.90 (m, 2H), 7.85–7.60 (m, 3H), 6.10–5.90 (m, 2H), 5.30–5.10 (m, 2H), 4.25–4.10 (m, 1H), 3.70–3.15 (m, 3H), 2.75–2.60 (m, 1H), 2.45–2.20 (m, 1H), 1.95–1.65 (m, 3H), 1.14 (br. signal, 1H), 0.90–0.82 (m, 1H). ^{13}C NMR (CD_3OD) δ 150.50; 149.04; 147.88; 137.90; 131.61; 129.58; 129.31; 126.40; 123.84; 120.33; 117.69; 69.04; 61.63; 50.80; 50.37; 38.23; 28.56; 23.96; 19.27.

2.1.3. Cinchonidine perrhenate salt (**III**)

IR (KBr disc) (cm^{-1}) 3320, 2950, 1500, 1450, 890, 860. ^{1}H-NMR (CD_3OD) δ 8.81 (br. s, 1H), 8.14–7.90 (m, 2H), 7.80–7.65 (m, 3H), 5.90 (s, 1H), 5.80–5.55 (m, 1H), 5.10–4.85 (m, 2H), 4.17 (br. signal, 1H), 3.70–3.40 (m, 2H), 3.35–3.10 (m, 2H), 2.72 (br. signal, 1H), 2.25–1.75 (br. m, 4H), 1.48 (br. signal, 1H). ^{13}C NMR (CD_3OD)



Scheme 2. Formation of perrhenate salt **IV** from reaction of MTO (or perrhenic acid) with (*R*)-1-phenylethylamine (**d**).



Scheme 3. Formation of perrhenate salt **V** from reaction of MTO (or perrhenic acid) with (*R*)-*N*,*N*-dimethyl-1-phenylethylamine (**e**).

δ 150.76; 148.77; 148.28; 139.04; 131.43; 129.94; 129.20; 126.35; 123.77; 120.41; 117.29; 68.76; 61.93; 55.83; 45.83; 38.43; 28.09; 25.18; 19.70.

2.1.4. (R)-1-Phenethylamine perrhenate salt (**IV**)

IR (KBr disc) (cm^{-1}) 3440, 3020, 1590, 1480, 890. ^{1}H-NMR (CD_3OD) δ 7.34 (s, 5H), 4.35 (q, $J = 7$ Hz, 1H), 1.52 (d, $J = 7$ Hz, 3H). ^{13}C NMR (CD_3OD) δ 139.48; 130.31; 130.20; 127.60; 52.39; 20.64.

2.1.5. (R)-N,N-Dimethylphenethylamine perrhenate salt (**V**)

IR (KBr disc) (cm^{-1}) 3410, 2970, 2700, 1440, 900, 855. ^{1}H-NMR (CD_3OD) δ 7.43 (s, 5H), 4.42 (q, $J = 7.2$ Hz, 1H), 2.80 (s, 3H), 2.64 (s, 3H), 1.66 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (CD_3OD) δ 136.00; 131.26; 130.51; 129.78; 67.60; 41.28; 16.42.

2.2. In situ ^{1}H and ^{13}C NMR analyses

For the amines (*R*)-1-phenylethylamine (**d**) and (*R*)-*N*,*N*-dimethyl-1-phenylethylamine (**e**), formation of the corresponding adducts with MTO was monitored by ^{1}H and ^{13}C NMR analyses. As a general procedure, to a 0.5-mL benzene-d_6 solution containing 0.1 mmol of MTO, 0.1 mmol of appropriate amine was added, at room temperature, and the sample was submitted to sequential ^{1}H and ^{13}C NMR analyses.

2.2.1. MTO/(R)-1-phenylethylamine adduct (not isolated)

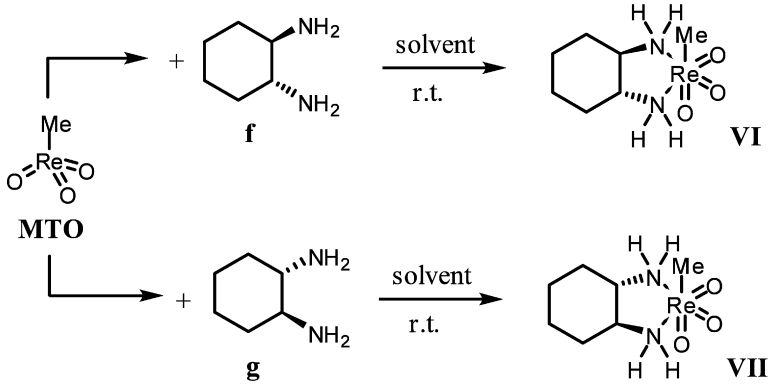
^{1}H-NMR (benzene-d_6) δ 6.95–6.85 (m, 3H), 6.70–6.60 (m, 2H), 3.49 (q, $J = 6.2$ Hz, 1H), 1.45 (br. s, 2H), 1.30 (s, 3H), 0.95 (d, $J = 6.2$ Hz, 3H). ^{13}C-NMR (benzene-d_6) δ 146.19; 129.51; 128.23; 126.72; 51.81; 25.81; 23.79.

2.2.2. MTO/(R)-N,N-Dimethylphenylethylamine adduct (not isolated)

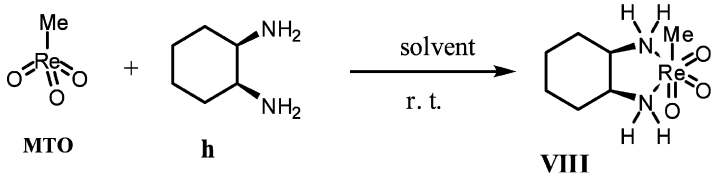
^{1}H-NMR (benzene-d_6) δ 7.07 (s, 5H), 3.26 (q, $J = 6.8$ Hz, 1H), 1.92 (s, 6H), 1.37 (s, 3H), 1.32 (d, $J = 6.8$ Hz, 3H). ^{13}C-NMR (benzene-d_6) δ 134.55; 128.86; 128.70; 128.38; 66.56; 43.25; 20.13; 17.56.

2.3. General procedure for the preparation of MTO/L_n adducts **VI–VIII**

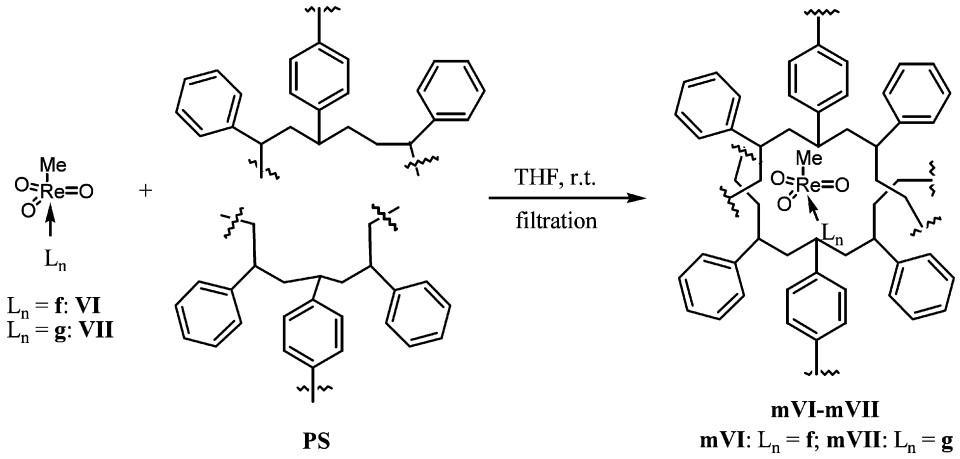
MTO/L_n adducts **VI**, **VII**, and **VIII**, containing the bidentate aliphatic amines *trans*-(1*R*,2*R*)-1,2-cyclohexyldiamine (**f**), *trans*-(1*S*,2*S*)-1,2-cyclohexyldiamine (**g**), and *cis*-1,2-cyclohexyldiamine (**h**), respectively, were prepared following a synthetic route described previously (Fig. 1, Schemes 4 and 5) [6]. In the general procedure, 0.2 mmol of the appropriate ligand was added to 0.2 mmol of MTO in toluene (2.0 mL) at room temperature. Rapid formation of a yellow precipitate was obtained in quantitative yield. Adducts **VI–VIII** were isolated by filtration, washed with *n*-hexane, and used with no further purification.



Scheme 4. Synthesis of MTO/L_n chiral adducts **VI–VII**.



Scheme 5. Synthesis of MTO/L_n chiral adduct **VIII**.



Scheme 6. Synthesis of heterogeneous chiral rhenium catalysts PS/MTO/L_n **mVI**–**mVII**.

2.3.1. MTO/(1R,2R)-1,2-diaminocyclohexane adduct (**VI**)

For ^{1}H- and ^{13}C-NMR spectra, see adduct **VII** below. Elemental analysis calcd (%) for $C_7H_{17}N_2O_3Re$: C, 23.13; H, 4.71; N, 7.71. Found: C, 23.60; H, 4.22; N, 7.85.

2.3.2. MTO/(1S,2S)-1,2-diaminocyclohexane adduct (**VII**)

^{1}H NMR (DMSO-d_6) δ 4.95–4.65 (br. signal, 2H), 3.95–3.55 (br. signal, 2H), 2.90–2.50 (br. signal, 1H), 2.50–2.10 (br. signal, 1H), 1.90–1.70 (m, 2H), 1.65–1.45 (m, 2H), 1.40–0.95 (m, 4H), 0.89 (s, 3H). ^{13}C-NMR (DMSO-d_6) δ 55.85, 33.63, 27.23, 24.43. Elemental analysis calcd (%) for $C_7H_{17}N_2O_3Re$: C, 23.13; H, 4.71; N, 7.71. Found: C, 23.87; H, 4.42; N, 7.75.

2.3.3. MTO/cis-1,2-diaminocyclohexane adduct (**VIII**)

^{1}H NMR (DMSO-d_6) δ 3.20–2.85 (br. signal, 4H), 2.27 (s, 3H), 1.70–0.70 (br signal, 10H). ^{13}C-NMR (DMSO-d_6) δ 51.96, 30.71, 27.68, 21.27. Elemental analysis calcd (%) for $C_7H_{17}N_2O_3Re$: C, 23.13; H, 4.71; N, 7.71. Found: C, 23.43; H, 4.37; N, 7.58.

2.4. General procedure for the preparation of microencapsulated MTO/L_n adducts **mVI** *and* **mVII**

Microencapsulated PS/MTO/L_n catalysts **mVI** and **mVII** were prepared following a modified procedure reported previously for the synthesis of polystyrene/MTO catalyst (Scheme 6) [7]. In brief, to a suspension of 100 mg of polystyrene (PS) in 2 mL of tetrahydrofuran (THF) was added 0.2 mmol of the appropriate MTO/L_n adduct **VI** or **VII** to obtain a value of the loading factor (i.e., mmol of MTO per g of support) of 2.0. Then the mixture was stirred for 1 h with a magnetic stirrer. Hexane (5.0 mL) was added to harden the capsule walls. Newly formed PS/MTO/L_n catalysts **mVI** and **mVII** were recovered by filtration, dried, and used with no further purification. In each case, the adducts **VI** and **VII** were completely bound to the polymer. This result was confirmed by spectroscopic analysis of the residue obtained after evaporation of the organic layers. The catalysts were used with no further purification.

2.5. Epoxidation of prochiral olefins **1**–**4**

2.5.1. Epoxidation with MTO/L_n adducts **VI**–**VIII**

At room temperature, to the solution of the appropriate catalyst (5.0% w/w) in 1.0 mL of solvent (CH_2Cl_2 or EtOH) was added the olefin (1.0 mmol) to be oxidized (Schemes 7 and 8) and an excess (3.0 equiv.) of oxidant (UHP). At the end of the reaction, a small amount of MnO_2 (2.0 mg) was added, to eliminate the excess of primary oxidant. The reaction mixture was found to be unchanged after the addition of MnO_2. The suspension was filtered, and the filtrate was dried over anhydrous Na_2SO_4. After the solvent evaporated, the crude product was analyzed by GC-MS and, when necessary, purified by flash-chromatography. Identity of products was confirmed by ^{1}H and ^{13}C NMR analyses. Spectra were compared with those of authenticated compounds.

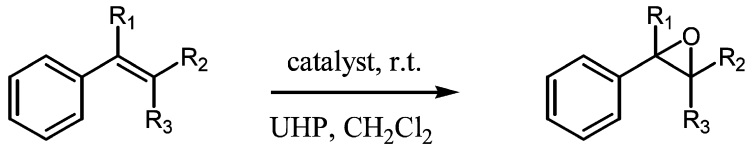
2.5.2. Epoxidation with microencapsulated PS/MTO/L_n adducts **mVI** *and* **mVII**

At room temperature, to the suspension of the appropriate catalyst **mVI** and **mVII** (5.0% w/w, loading factor 2.0) in 1.0 mL of solvent (CH_2Cl_2 or EtOH) was added the olefin (1.0 mmol) to be oxidized (Schemes 7 and 8) and an excess (3.0 equiv.) of UHP. At the end of the reaction, the catalyst was recovered by filtration and washed with CH_2Cl_2. A small amount of MnO_2 (2.0 mg) was added to eliminate the excess of primary oxidant. Then the suspension was filtered once again, with the filtrate dried over anhydrous Na_2SO_4. After the solvent evaporated, the crude product was analyzed by GC-MS and, when necessary, purified by flash-chromatography. Identity of products was confirmed by ^{1}H and ^{13}C NMR analyses. Spectra were compared with those of authenticated compounds.

3. Results and discussion

3.1. Synthesis and characterization of MTO/L_n adducts between MTO and aliphatic amines: Effects of the ligand and the reaction solvent

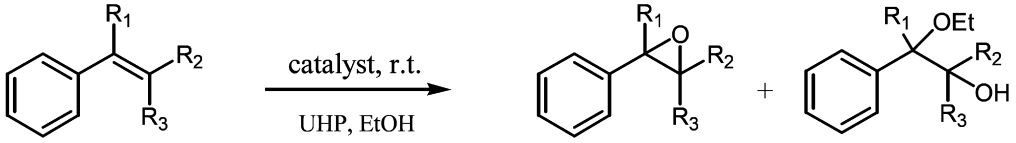
Chiral monodentate and bidentate aliphatic amines **a**–**h** (Fig. 1) were used for the synthesis of MTO/L_n adducts, following a synthe-



1-3 **6a-c**

$R_1 = R_2 = R_3 = H$: styrene **1**
$R_1 = Me$; $R_2 = R_3 = H$: α-methylstyrene **2**
$R_1 = R_2 = H$; $R_3 = Me$: *cis*-β-methylstyrene **3**

Scheme 7. Catalytic epoxidation of olefins **1**–**3**, in dichloromethane.



1-4 **6a, 6c-d** **7a-b**

$R_1 = R_2 = R_3 = H$: styrene **1**
$R_1 = Me$; $R_2 = R_3 = H$: α-methylstyrene **2**
$R_1 = R_2 = H$; $R_3 = Me$: *cis*-β-methylstyrene **3**
$R_1 = R_2 = H$; $R_3 = Ph$; *cis*-stylbene **4**

Scheme 8. Catalytic epoxidation of olefins **1**–**4**, in ethanol.

sis procedure reported previously [5a,6]. In particular, the alkaloids hydrocinchonine (**a**), cinchonine (**b**), and cinchonidine (**c**) did not yield the corresponding MTO/L_n adducts, irrespective of the use of nonpolar solvents, such as toluene or benzene, or slightly more polar solvents, such as tetrahydrofuran (THF) or dioxane, working either at room temperature or lower temperatures. The hindrance at the tertiary nitrogen atom of the quinuclidine ring likely prevented the formation of isolable adducts. Any attempt to force the experimental conditions led to the decomposition of MTO with formation of the corresponding perrhenate salts **I**–**III** (Scheme 1, path 1). These compounds did not exhibit the Re–CH_3 signal in their ^{1}H-NMR spectra but did have the characteristic symmetric and asymmetric ν(Re=O) stretching vibration mode at ca. 900 cm^{-1} in their FT-IR spectra. The structure of perrhenate salts **I**–**III** was unambiguously assigned through comparison with authenticated samples prepared by reaction of amines **a**–**c** with perrhenic acid (Scheme 1, path 2). The reaction of (*R*)-1-phenylethylamine (**d**) with MTO was monitored by *in situ* ^{1}H NMR spectroscopy in benzene-d_6 at 25 °C and compared with the spectra of authenticated samples of both amine (**d**) and MTO recovered under similar experimental conditions. The presence of a downfield shift for both the NH_2 protons ($\Delta\delta$ +0.82 ppm) and $ReCH_3$ group (^{1}H NMR: $\Delta\delta$ +0.30 ppm; ^{13}C NMR: $\Delta\delta$ +6.69 ppm) and of an upfield shift for two aromatic protons ($\Delta\delta$ −0.18 ppm) suggested the formation of the MTO/(**d**) complex. Unfortunately, any attempt to isolate this complex led only to the formation of a dark-brown, sticky gum containing, along with perrhenate salt **IV** (Scheme 2, path 1), other unidentified side products likely derived from the known oxidation processes of primary amines in the presence of rhenium catalysts [8]. In the case of (*R*)-*N*,*N*-dimethyl-1-phenylethylamine (**e**), rapid decomposition of the MTO/(**e**) adduct to perrhenate salt **V** was observed, probably due to the high basic character of the tertiary amine (**e**) (Scheme 3, path 1). Again, the structures of perrhenate salts **IV** and **V** were unambiguously assigned through comparison with authenticated samples prepared by reaction of amines (**d**) and (**e**) with perrhenic acid (Schemes 2 and 3, path 2).

Of note, the addition of enantiomeric *trans*-(1*R*,2*R*)-1,2-cyclohexyldiamine (**f**) and *trans*-(1*S*,2*S*)-1,2-cyclohexyldiamine (**g**) to an equimolar amount of MTO in toluene at room temperature resulted in the rapid formation of a pale-yellow precipitate, with the corresponding MTO/L_n adducts **VI** and **VII** recovered in quantitative yield (Scheme 4). The adducts **VI** and **VII** were fully characterized by spectroscopic and spectrometric analyses. These compounds were found to be stable for longer than 6 months when stored at 4 °C. To better investigate the effect of the configuration of the diamino moiety on the formation of stable MTO/L_n adducts, we also studied the reaction of MTO with the isomeric *meso* form *cis*-1,2-cyclohexyldiamine (**h**). In this latter case, the MTO/(**h**) adduct **VIII** also was recovered from the reaction mixture as a pale-yellow precipitate in quantitative yield (Scheme 5).

These data indicate that irrespective of the stereochemistry of the amino ligand, the 1,2-diamino moiety was a crucial requirement for stable and recoverable MTO/L_n adducts. To the best of our knowledge, this is the first study reported to date dealing with the preparation, isolation, and characterization of stable and easily recoverable MTO adducts with aliphatic amines. Of most relevance appears to be the possibility of synthesizing stable chiral MTO complexes. The chiral adducts **VI** and **VII** also have been used for the successive preparation of MTO heterogeneous catalysts.

3.2. Synthesis and characterization of heterogeneous chiral rhenium catalysts PS/MTO/L_n based on microencapsulation of MTO/L_n VI and VII adducts in polystyrene

The chiral heterogeneous catalysts were prepared by microencapsulation of MTO/L_n **VI** and **VII** adducts in polystyrene (Scheme 6) [7b]. A set of scanning electron microscopy (SEM) photographs showing the morphology of the surface of particles of catalysts **mVI** and **mVII** are reported in Figs. 2–4. Compounds **mVI** and **mVII** are characterized by particles with a regular spherical shape, with an average value of diameter of the order of 50 μm. Small numbers of irregular fragments were observed for both catalysts, likely due to mechanical damage of particles during sample preparation. At higher magnification, the particles of **mVI** exhibit a dense sheet paving formed by a compact aggregate of small spherical grumes.

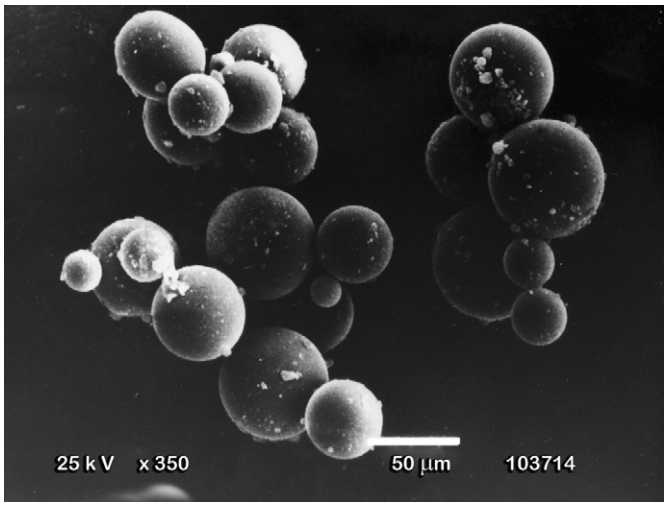


Fig. 2. Scanning electron microscopy (SEM) micrograph of **mVI** catalyst.

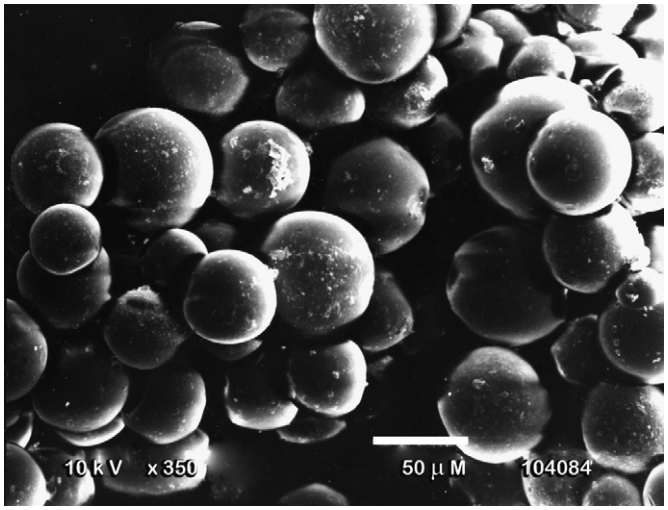


Fig. 3. Scanning electron microscopy (SEM) micrograph of **mVII** catalyst.

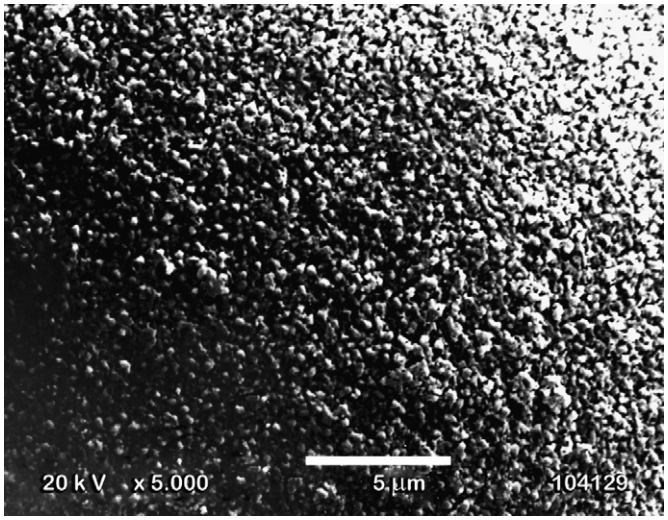


Fig. 4. Scanning electron microscopy (SEM) micrograph of **mVI** catalyst at largest magnification.

Table 1
Selected vibrational frequencies [ν(ReO)] of catalysts **VI**, **VII**, **VIII**, **mVI** and **mVII**[a]

Catalyst	[ν(ReO)] cm^{-1}
VI	897.0; 837.0
VII	896.5; 836.5
VIII	898.0; 837.0
mVI	896.2; 839.6
mVII	896.5; 840.0

[a] Data recovered at room temperature.

Table 2
Oxidation of olefins **1**–**3** in CH_2Cl_2 with UHP and MTO/L_n adducts **VI**–**VIII** or microencapsulated PS/MTO/L_n adducts **mVI** and **mVII**

Entry	Olefin	Catalyst[a]	Conv. (%)	Product[b]	Yield(s)[c] (%)
1	**1**	**MTO**	78	**6a**	70[d]
2	**1**	**VI**	72	**6a**	72
3	**2**	**VI**	35	**6b**	30
4	**3**	**VI**	74	**6c**	73
5	**1**	**VII**	78	**6a**	72
6	**2**	**VII**	38	**6b**	34
7	**3**	**VII**	78	**6c**	76
8	**1**	**VIII**	39	**6a**	39
9	**2**	**VIII**	37	**6b**	37
10	**3**	**VIII**	55	**6c**	55
11	**1**	**mVI**	54	**6a**	52
12	**3**	**mVI**	68	**6c**	65
13	**1**	**mVII**	56	**6a**	54
14	**3**	**mVII**	70	**6c**	68

[a] Catalysts: MTO/(1*R*,2*R*)-1,2-cyclohexyldiamine, **VI**; MTO/1*S*,2*S*)-1,2-cyclohexyldiamine, **VII**; MTO/*cis*-1,2-cyclohexyldiamine, **VIII**; microencapsulated MTO/(1*R*,2*R*)-1,2-cyclohexyldiamine, **mVI**; microencapsulated MTO/(1*S*,2*S*)-1,2-cyclohexyldiamine, **mVII**.
[b] The reactions were performed in CH_2Cl_2, UHP (3 equiv.), 5% w/w of catalyst, at r.t., running for 24 h.
[c] The yields are referred to mmol of product per mmol of starting material.
[d] Phenylacetaldehyde (8% yield) was also detected in the reaction mixture.

Because the assignment of the vibrational frequencies of the R–ReO_3 and R–ReO_3/ligand systems has been described previously, IR spectroscopy is also useful for analyzing novel MTO complexes [9]. Table 1 gives the values recovered for the ν(ReO) stretching vibration modes of catalysts **VI**, **VII**, **VIII**, **mVI**, and **mVII** as revealed by ATR-IR spectroscopic analysis. All of the complexes have lower ν(ReO) frequencies compared with MTO, equal to 998 cm^{-1} for the symmetric stretching vibration mode and to 959 cm^{-1} for the asymmetric stretching vibration mode [10]. These data are in accordance with findings reported previously for both homogeneous and heterogeneous MTO complexes.

3.3. *Epoxidation of olefins with MTO/L_n adducts* **VI**–**VIII** *and microencapsulated PS/MTO/L_n heterogeneous catalysts* **mVI** *and* **mVII**

Table 2 and Scheme 7 summarize the epoxidation of a panel of prochiral olefins as styrene **1**, α-methylstyrene **2**, and *cis*-β-methyl styrene **3** with MTO/L_n adducts **VI**–**VIII** or microencapsulated PS/MTO/L_n heterogeneous catalysts **mVI** and **mVII**, using the urea hydrogen peroxide adduct as the primary oxidant. Irrespective of experimental conditions, the epoxide was the only product recovered besides unreacted substrate. High mass balance values were seen, in accordance with complete selectivity of the oxidation. The epoxidation of olefin **1** with MTO also was performed as a reference. In accordance with data reported previously in the literature on the reactivity of rhenium derivatives, very low conversion of substrate (<3%) was obtained when perrhenate salts **I**–**V** were used as catalysts, even under forced experimental conditions (i.e., high temperature and large excess of the primary oxidant) [11]. In particular, the oxidation of **1** with **VI** afforded the epoxide

Table 3
Oxidation of olefins **1**–**4** in EtOH with UHP and MTO/L_n adducts **VI**–**VIII** or microencapsulated PS/MTO/L_n adducts **mVI** and **mVII**

Entry	Olefin	Catalyst[a]	Conv. (%)	Product(s)[b]	Yield(s) (%)[c,d]
1	**1**	**MTO**	99	**6a**, **7a**	56 (44)
2	**1**	**VI**	99	**6a**, **7a**	70 (28)
3	**2**	**VI**	99	**7b**	98
4	**3**	**VI**	99	**6c**	98
5	**1**	**VII**	99	**6a**, **7a**	72 (27)
6	**2**	**VII**	99	**7b**	98
7	**3**	**VII**	99	**6c**	98
8	**1**	**VIII**	72	**6a**, **7a**	47 (25)
9	**2**	**VIII**	87	**7b**	87
10	**3**	**VIII**	88	**6c**	88
11	**4**	**VII**	97	**6d**	96
12	**1**	**mVI**	82	**6a**, **7a**	75 (7)
13	**2**	**mVI**	78	**7b**	76
14	**3**	**mVI**	99	**6c**	99
15	**1**	**mVII**	85	**6a**, **7a**	78 (6)
16	**2**	**mVII**	88	**7b**	86
17	**3**	**mVII**	99	**6c**	99
18	**4**	**mVII**	85	**6d**	83

[a] Catalysts: MTO/(1*R*,2*R*)-1,2-cyclohexyldiamine, **VI**; MTO/(1*S*,2*S*)-1,2 cyclohexyldiamine, **VII**; MTO/*cis*-1,2-cyclohexyldiamine, **VIII**; microencapsulated MTO/(1*R*,2*R*)-1,2-cyclohexyldiamine, **mVI**; microencapsulated MTO/(1*S*,2*S*)-1,2-cyclohexyldiamine, **mVII**.
[b] The reactions were performed in EtOH, UHP (3 equiv.), 5% w/w of catalyst, at r.t., running for 24 h.
[c] Yields in parentheses are referred to product **7a**.
[d] The yields are referred to mmol of product per mmol of starting material.

6a in acceptable conversion of substrate and high yield (Table 2, entry 2). Catalyst **VI** was more selective than MTO; in fact, byproducts, such as phenylacetaldehyde, previously observed during the oxidation with MTO (Table 2, note d), were not recovered in the reaction mixture (Table 2, entry 2 versus entry 1). The position of the methyl group on the isomeric olefins **2** and **3** (i.e., the α- vs β-position on the vinyl moiety) played a relevant role in the efficiency of the oxidation. Thus, although a low conversion of substrate and a low yield of epoxide **6b** were recovered from the oxidation of **2**, the oxidation of **3** afforded the epoxide **6c** in high conversion and yield (Table 2, entry 4 vs entry 3). Similar results were obtained in the oxidations with **VII**, with epoxides **6a** and **6c** isolated at yields (72% and 76%, respectively) greater than that of **6b** (Table 2, entries 5–7). As a general reaction pattern, catalyst **VIII** exhibited poorer performance compared with catalysts **VI** and **VII** (Table 2, entries 8–10).

The oxidations with microencapsulated PS/MTO/L_n were successively performed with the most reactive catalysts, **mVI** and **mVII**, and olefins **1** and **3**. It is interesting to note that both catalysts afforded epoxides **6a** and **6c** in yields comparable to that of their homogeneous counterpart, with olefin **3** being the most reactive substrate (see, e.g., Table 2, entries 11 and 12 vs 2 and 4). Thus, specific kinetic barriers to the approach of substrate to heterogeneous systems were not observed. To the best of our knowledge, this is the first report dealing with the high efficacy of aliphatic amines in tuning the reactivity of MTO, both in homogeneous and heterogeneous conditions. This reactivity is comparable to that reported previously for aromatic amines [12].

3.4. Effect of solvent on epoxidation

It is well known from the literature that the reactivity of MTO can be increased by the use of polar protic solvents, such as alcohols [1a,13]. Based on these data, and with the aim of increasing the conversion of substrate, we repeated the oxidation of olefins **1**–**3** with MTO/L_n adducts **VI**–**VIII** and PS/MTO/L_n adducts **mVI** and **mVII** in ethanol (EtOH) under similar experimental conditions. In this latter case, the *cis*-stylbene **4** also was evaluated as a substrate under selected conditions (Table 3 and Scheme 8). Because EtOH is a nucleophilic solvent, these oxidations were useful probes for evaluating the stability of newly formed epoxides toward possible solvolytic side processes. The results of the oxidations are reported in Table 3 and Scheme 8. Again, the yields are referred to mmol of product per mmol of starting material. The oxidation of **1** with **VI** in EtOH proceeded with a quantitative conversion of substrate (greater than that observed previously in CH_2Cl_2) to give a mixture of **6a** as the main reaction product (70%) and of the oxiranyl ring-opened derivative **7a** (28%) as a side product (Table 3, entry 2). Similar behavior was observed in the oxidation of **1** with **VII** and **VIII** (Table 3, entries 5 and 8, respectively). Of note, the yield of **6a** with catalysts **VI** and **VII** was higher than that obtained with MTO (see, e.g., Table 3, entry 2 vs entry 1), with **VII** being the most efficient system. These data further confirm the capability of aliphatic amines of tuning the reactivity of MTO. Irrespective of experimental conditions, the oxidation of olefin **2** always afforded the ring-opened derivative **7b** in high or quantitative yield (Table 3, entries 3, 6, and 9). In contrast, a quantitative conversion of **3** and a quantitative yield of epoxide **6c** was obtained with catalysts **VI** and **VII** (Table 3, entries 4 and 7), with catalyst **VIII** showing a slightly lower reactivity (Table 3, entry 10). Finally, when olefin **4** was treated with **VII**, a quantitative conversion of substrate and quantitative yield of *cis*-stylbene oxide **6d** was obtained (Table 3, entry 11). It is interesting to note that the oxidation of **1** with microencapsulated catalyst **mVII** afforded **6a** in higher yield and better selectivity than obtained with catalyst **VII** (Table 3, entry 12 vs entry 2), thus suggesting a role of the microcapsule environment in the oxidation pathway. These data are in accordance with our previous findings on the effect of the polymeric matrix on the reactivity and selectivity of MTO [4]. Again, irrespective of the catalyst used, the oxidation of **2** always afforded **7b** as the sole recovered product, with **mVII** being the most reactive system (Table 3, entries 13 and 16). Of note, a quantitative conversion of substrate and a quantitative yield of epoxide **6c** were obtained in the oxidation of **3** with both catalysts **mVI** and **mVII** (Table 3, entries 14 and 17). The catalyst **mVII** also proved to be an efficient system for the oxidation of **4** to give **6d** in high yield (Table 3, entry 18).

3.5. Evaluation of stereoselectivity for the epoxidation of prochiral olefins

Despite the high reactivity and versatility of MTO in the epoxidation of olefins, up to now, no relevant results in terms of stereoselectivity have been obtained. To date, efforts have focused mainly on using MTO in the presence of a large excess of chiral amines added to the reaction mixture; for example, Corma et al. [14] reported moderate stereoinduction values (accompanied by low conversion values) during the epoxidation of prochiral olefins at low temperature (from $-5\,^{\circ}C$ to $-55\,^{\circ}C$), with MTO and added chiral amines. Similar results have been reported by Herrmann and Kühn et al. [1b,15] in the MTO-catalyzed epoxidation of prochiral olefins in the presence of a large excess of chiral pyrazole based ligands. In this latter case, the fluxionality property of MTO nitrogen-based adducts (i.e., the rapid equilibrium between the coordinated and the noncoordinated species) was suggested to explain the effect of the temperature on the values of stereoinduction [1b,15]. With the aim of evaluating the values of stereoselectivity induced by our chiral MTO complexes, the epoxidation of **1** with **VI** and **mVI**, performed in both CH_2Cl_2 and EtOH, was analyzed by GC in a chiral capillary column (30 m × 0.25 mm × 0.25 μm film thickness BETA-DEX-325 fused silica) as selected representative examples. The results, collected in Table 4, show rather low ee in the oxidation of **1** with **VI** in both reaction solvents (Table 4, entries 1 and 2). In contrast, the use of **mVI** as the catalyst led to a signif-

Table 4
Asymmetric epoxidation of styrene **1** catalyzed by compounds **VI** and **mVI**

Entry	Catalyst	Solvent	Conversion (%)	ee (%)[a]	Yield of epoxide (%)
1	**VI**	CH_2Cl_2	72	15	72
2	**VI**	EtOH	99	13	70
3	**mVI**	CH_2Cl_2	54	20	52
4	**mVI**	EtOH	82	24	75

[a] The ee was evaluated by gas-chromatography in a chiral capillary column (30 m × 0.25 mm × 0.25 μm film thickness BETA-DEX-325 Fused Silica).

icant improvement in enantioselectivity, with the highest ee values obtained in EtOH (Table 4, entries 3 and 4). Based on these data, it is reasonable to suggest that the microencapsulation process was able to tune the reactivity of **VI**, probably by shifting the dynamic equilibrium of the activated complex toward the coordination of the chiral amine to the rhenium atom. To the best of our knowledge, the results obtained with **mVI** are the highest values of enantioselectivity reported so far for the epoxidation of prochiral olefins with MTO adducts at room temperature and with high conversion of substrate and yield of product.

4. Conclusion

Herein we report that chiral aliphatic amines can be efficiently used to synthesize novel MTO/L_n adducts and microencapsulated PS/MTO/L_n catalysts able to retain the reactivity of MTO in the epoxidation of olefins with UHP. These compounds exhibited a reactivity similar to that reported previously for MTO in the presence of aromatic amines. A basic difference can be drawn, however; whereas a large excess of aromatic amines is required to optimize the reactivity of MTO, only a stoichiometric ratio of ligand can be used in the case of aliphatic amines. Moreover, synthetic and natural aliphatic amines are available to synthesize a large panel of novel chiral MTO catalysts. In particular, we have described for the first time the preparation of adducts MTO/L_n between MTO and chiral bidentate aliphatic amines, noting that the coordination property of the ligand was a crucial factor in the stability of the adduct (i.e., bidentate vs monodentate aliphatic amines). Novel heterogeneous catalysts, PS/MTO/L_n, based on the microencapsulation of chiral MTO/L_n adducts on polystyrene, also have been prepared. The catalytic behavior of homogeneous MTO/L_n adducts **VI**–**VIII** and microencapsulated heterogeneous catalysts **mVI** and **mVII** in the epoxidation of several prochiral olefins with UHP have been investigated in depth under different experimental conditions. As a general reaction pattern, catalysts **VI** and **VII** showed the highest reactivity and selectivity, especially in when ethanol was used as the solvent, affording quantitative conversion of substrate and yield of epoxide in different cases. The microencapsulated catalysts **mVI** and **mVII** behaved similarly, thus suggesting the absence of a kinetic barrier in the approaching step of substrate toward active rhenium species. In terms of stereoselectivity, moderate ee values were obtained during the oxidation of styrene **1** with catalyst **VI**. It is noteworthy that the microencapsulation process increased the stereoinduction values.

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