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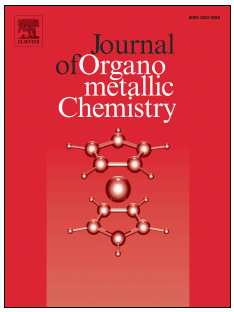

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Performance of chiral tetracarbonylmolybdenum pyrindanyl amine complexes in catalytic olefin epoxidation

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ABSTRACT

Tetracarbonylmolybdenum(0) complexes of the type *cis*-[Mo(CO)$_4$(L)] containing chiral 7-(1-pyrindanyl) amine ligands were prepared and found to be effective precatalysts for the epoxidation of achiral (*cis*-cyclooctene) and prochiral (DL-limonene and *trans*-β-methylstyrene) olefins at 55 ºC. Epoxides were the only products formed from *cis*-cyclooctene (100% yield) and *trans*-β-methylstyrene (100% selectivity at 82-85% conversion), and the main products formed from DL-limonene (80-82% 1,2-epoxide selectivity at 85% conversion). Characterization of recovered catalysts revealed that the precatalysts were transformed *in situ* to stable polyoxomolybdate salts containing the β-octamolybdate anion [β-Mo_8O_{26}]$^{4-}$, which was responsible for the catalytic reaction.

Keywords: Molybdenum; Tetracarbonyl complexes; Olefin epoxidation; Chiral ligands; 1-pyrindane derivatives; Oxidative decarbonylation

1. Introduction

The family of group 6 metal carbonyl complexes is versatile and effective for several catalytic reactions such as hydrogenation, hydrosilylation, hydrogermylation, hydroxylation, isomerization, olefin metathesis and metathesis polymerization, radical reactions, and (ep)oxidation (e.g. of alkenes, amines, alcohols and sulfides) [1-5]. The application of these carbonyl complexes in catalysis first arose in the late 1960's [6,7] with the use of $Mo(CO)_6$ as a precatalyst for the epoxidation of olefins (monoolefins [6], diolefins and functionalized olefins [7]), using an organic hydroperoxide as oxidant, namely *tert*-butylhydroperoxide (TBHP) or cumene hydroperoxide. Halcon (later Oxirane, Arco Chemical, and Lyondell Petrochemical [7]) claimed the application of $Mo(CO)_6$ for the industrial catalytic production of the bulk chemical propylene oxide, which is used in a variety of plastics, foams and paints [3,8-10]. More recently, in 2007, Dow Global Technologies Inc. claimed the application of various families of molybdenum compounds as homogeneous catalysts to produce epoxides via liquid-phase reaction of olefins with organic hydroperoxides [11].

Since the turn of the century, there has been growing interest in the use of molybdenum carbonyl complexes as precursors to Mo^{VI} catalysts for oxidation reactions, with most of the research being focused on dicarbonyl and tricarbonyl complexes [2-5,12-14]. From 2010 onwards some of us have been investigating tetracarbonyl complexes of the type *cis*-$[Mo(CO)_4L]$ (L = *N*,*N*-ligand) for the epoxidation of aliphatic and cyclic olefins (e.g. terpenes), using TBHP as oxidant [15-19]. The Mo^0 complexes can be used directly as catalyst precursors since they undergo oxidative decarbonylation *in situ* (by reaction with the oxidant) to give oxomolybdenum compounds in higher (usually +6) oxidation states. A variety of oxidized compounds have been isolated and include the one-dimensional molybdenum oxide/bipyridine polymer $[MoO_3(2,2'\text{-bipy})]$ from *cis*-$[Mo(CO)_4(2,2'\text{-bipy})]$ (2,2'-bipy = 2,2'-bipyridine) [15], the octanuclear cluster $[Mo_8O_{24}(\text{di-}t\text{Bu-bipy})_4]$ from *cis*-$[Mo(CO)_4(\text{di-}t\text{Bu-bipy})]$ (di-*t*Bu-bipy = 4,4'-di-*tert*-butyl-2,2'-bipyridine) [15], and the tetranuclear species $[Mo_4O_{12}(\text{pypzH})_4]$ from *cis*-$[Mo(CO)_4(\text{pypz})]$ (pypzH = 2-[3(5)-pyrazolyl]pyridine) [16].

To the best of our knowledge, tetracarbonylmolybdenum complexes containing chiral organic ligands have not yet been studied in catalytic olefin epoxidation. Herein we report on the synthesis of two chiral tetracarbonylmolybdenum pyrindanyl amine complexes and their use as precatalysts for the epoxidation of *cis*-cyclooctene (used as a benchmark substrate),

DL-limonene and *trans*-β-methylstyrene. The catalytic performances of the complexes are compared with results reported previously for related complexes. Characterization of recovered catalysts established that the tetracarbonyl complexes are oxidized to octamolybdate salts of the type $(LH)_4[Mo_8O_{26}]$ (rather than to hybrid complexes or materials where the organic ligand remains coordinated to the metal center, which has been reported in the literature for different tetracarbonylmolybdenum organo complexes).

2. Experimental

2.1. Materials and methods

Molybdenum hexacarbonyl (Fluka), *cis*-cyclooctene (95%, Alfa Aesar), DL-limonene (≥95%, Merck), *trans*-β-methylstyrene (99%), *tert*-butylhydroperoxide (5.0-6.0 M in decane), α,α,α-anhydrous trifluorotoluene (≥99%), anhydrous acetonitrile (99.8%), hexane (99%), 1,2-dichloroethane (99%), *n*-pentane (>95%, Carlo Erba), diethyl ether (99.8%), undecane (99%), (*R*)-(+)-α-methylbenzylamine (98%), (*S*)-(−)-α-methylbenzylamine (98%), 37% formaldehyde solution, and sodium triacetoxyborohydride (97%) were purchased from Sigma-Aldrich unless otherwise indicated, and used as received.

Microanalyses for C, H and N were carried out at the Department of Chemistry, University of Aveiro, with a Truspec Micro CHNS 630-200-200 elemental analyzer. FT-IR spectra in the 300−4000 cm^{-1} range were collected using KBr (Sigma-Aldrich, 99%, FT-IR grade) pellets and a Mattson-7000 infrared spectrophotometer. Attenuated total reflectance (ATR) FT-IR spectra were measured using a Specac Golden Gate Mk II ATR accessory having a diamond top plate and KRS-5 focusing lenses (256 scans, resolution 4 cm^{-1}). Solution ^{1}H and ^{13}C NMR spectra were measured with Bruker CXP 300 (Department of Chemistry, University of Aveiro), Avance-300 (Department of Chemistry, University of Aveiro) or Avance III 400 (Centro de Materiais da Universidade do Porto – CEMUP) instruments. Chemical shifts are quoted in ppm from TMS. Mass spectra were recorded on a LTQ Orbitrap XL mass spectrometer (Thermo Fisher Scientific, Bremen, Germany) controlled by LTQ Tune Plus 2.5.5 and Xcalibur 2.1.0 (CEMUP). Optical rotations were measured on a thermostated Jasco P-2000 digital polarimeter using a sodium lamp. Flash chromatography was performed on silica gel (Merck 60, 230–240 mesh), and analytical TLC was carried out on pre-coated silica gel plates (Merck 60 F_{254}, 0.25 mm) using UV light

and/or an ethanolic solution of phosphomolybdic acid (followed by gentle heating) for visualization.

2.2. Synthesis

2.2.1. General protocol for reductive amination

In a round bottomed flask, the appropriate amine was dissolved in anhydrous CH_2Cl_2 (20 mL) followed by addition of anhydrous Na_2SO_4 and the carbonyl compound (ketone **3** or formaldehyde) (Scheme 1). The reaction was left under magnetic stirring for 4 h at room temperature. After that period, the reducing agent, $NaBH(OAc)_3$, was carefully added and the reaction allowed to proceed for a further 20 h. The reaction mixture was filtered under reduced pressure and saturated $NaHCO_3$ (20 mL) was added to the filtrate. The phases were transferred to a separating funnel and the aqueous phase was washed with CH_2Cl_2 (3 × 20 mL). The organic extracts were combined and dried over anhydrous Na_2SO_4, filtered, and the solvent removed *in vacuo*. The crude oil was chromatographed using AcOEt as eluent, affording the desired amine.

*2.2.1.1. (R,R)-N-(1-phenylethyl)-6,7-dihydro-5H-cyclopenta[b]pyridin-7-amine (**4**)*

Following the general protocol for reductive amination, (*R*)-(+)-α-methylbenzylamine (0.73 mL, 5.6 mmol) was reacted with ketone **3** (0.500 g, 3.75 mmol) and $NaBH(OAc)_3$ (1.193 g, 5.63 mmol). After the work-up procedure and purification, amine **4** was obtained as a brown oil (0.715 g, 80%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.40 (d, *J* = 4.9 Hz, 1H, H-2), 7.50–7.39 (m, 3H, ArH), 7.35–7.28 (m, 2H, ArH), 7.27–7.20 (m, 1H, ArH), 7.05 (dd, *J* = 7.5, 5.0 Hz, 1H, H-3), 4.24 (q, *J* = 6.6 Hz, 1H, NHC<u>H</u>(CH_3)Ph), 4.12 (t, *J* = 7.7 Hz, 1H, H-7), 2.79 (ddd, *J* = 16.1, 8.9, 2.9 Hz, 1H, H-5$_{syn}$), 2.68–2.57 (m, 1H, H-5$_{anti}$), 2.53 (br s, 1H, NH), 1.97 (dtd, *J* = 12.8, 7.8, 3.0 Hz, 1H, H-6$_{syn}$), 1.58 (ddd, *J* = 17.1, 12.8, 8.9 Hz, 1H, H-6$_{anti}$), 1.47 (d, *J* = 6.6 Hz, 3H, NHCH(C<u>H</u>$_3$)Ph) (see Fig. 1 for atom labelling). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 165.5 (C-7a), 147.8 (CH, C-2), 146.5 (C, C$_{ipso}$), 136.5 (C, C-4a), 132.6 (CH, C-4), 128.4 (2CH, 2 × C$_{meta}$), 127.4 (2CH, 2 × C$_{ortho}$), 127.1 (CH, C$_{para}$), 122.2 (CH, C-3), 62.5 (CH, C-7), 58.7 (CH, NH<u>C</u>H(CH_3)Ph), 33.8 (CH_2, C-6), 28.3 (CH_2, C-5), 24.4 (CH_3, NHCH(<u>C</u>H_3)Ph). ESI-MS: calculated for $[C_{16}H_{19}N_2]^+$, 239.15; obtained, 239.19. $\alpha_D^{20\,°C} = +28.6$ (*c*1, $CHCl_3$).

*2.2.1.2. (S,S)-N-(1-phenylethyl)-6,7-dihydro-5H-cyclopenta[b]pyridin-7-amine (**5**)*

Following the general protocol for reductive amination, (*S*)-(−)-α-methylbenzylamine (0.73 mL, 5.6 mmol) was reacted with ketone **3** (0.500 g, 3.75 mmol) and $NaBH(OAc)_3$ (1.193 g, 5.63 mmol). After the work-up procedure and purification, amine **5** was obtained as a brown oil (0.751 g, 84%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.40 (d, *J* = 4.9 Hz, 1H, H-2), 7.50–7.41 (m, 3H, ArH), 7.36–7.28 (m, 2H, ArH), 7.27–7.20 (m, 1H, ArH), 7.05 (ddd, *J* = 7.5, 4.9, 0.4 Hz, 1H, H-3), 4.25 (q, *J* = 6.6 Hz, 1H, NHC<u>H</u>(CH_3)Ph), 4.12 (t, *J* = 7.7 Hz, 1H, H-7), 2.80 (ddd, *J* = 16.1, 8.8, 2.9 Hz, 1H, H-5$_{syn}$), 2.73–2.45 (m, 2H, H-5$_{anti}$ + NH), 1.97 (dtd, *J* = 12.8, 7.8, 3.0 Hz, 1H, H-6$_{syn}$), 1.60 (ddd, *J* = 17.1, 12.8, 8.8 Hz, 1H, H-6$_{anti}$), 1.48 (d, *J* = 6.6 Hz, 3H, NHCH(C<u>H</u>$_3$)Ph). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 165.2 (C, C-7a). 147.8 (CH, C-2), 146.0 (C, C$_{ipso}$), 136.7 (C, C-4a), 132.7 (CH, C-4), 128.8 (2 × CH, ArC), 127.5 (2 × CH, ArC), 127.2 (CH, ArC), 122.3 (CH, C-3), 62.3 (CH, C-7), 58.6 (CH, NH<u>C</u>H(CH_3)Ph), 33.6 (CH_2, C-6), 28.2 (CH_2, C-5), 24.5 (CH_3, NHCH(<u>C</u>H$_3$)Ph). ESI-MS: calculated for $[C_{16}H_{19}N_2]^+$, 239.15; obtained, 239.39. $\alpha_D^{20\,℃} = -27.9$ (*c*1, $CHCl_3$).

*2.2.1.3. (R,R)-N-methyl-N-(1-phenylethyl)-6,7-dihydro-5H-cyclopenta[b]pyridin-7-amine [(R,R)-pyC_5H_5N(CH_3)CH(CH_3)Ph=**L1**]*

Following the general protocol for reductive amination, amine **4** (0.700 g, 2.94 mmol) was reacted with an aqueous 37% solution of formaldehyde (0.33 mL, 4.4 mmol) and $NaBH(OAc)_3$ (1.869 g, 8.82 mmol). After the work-up procedure and purification, amine **L1** was obtained as a brown oil (0.579 g, 78%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.60–8.38 (m, 1H, H-2), 7.55–7.48 (m, 2H, ArH), 7.45 (dd, *J* = 7.6, 1.3 Hz, 1H, ArH), 7.35–7.28 (m, 2H, ArH), 7.26–7.20 (m, 1H, ArH), 7.05 (dd, *J* = 7.5, 4.9 Hz, 1H, H-3), 4.57 (t, *J* = 7.7 Hz, 1H, H-7), 4.16 (d, *J* = 5.0 Hz, 1H, N(CH_3)C<u>H</u>(CH_3)Ph), 2.88 (ddd, *J* = 16.2, 8.8, 4.7 Hz, 1H, H-5$_{syn}$), 2.74 (ddd, *J* = 16.2, 8.4, 7.7 Hz, 1H, H-5$_{anti}$), 2.14–1.93 (m, 5H, H-6$_{syn}$ + H-6$_{anti}$ + N(C<u>H</u>$_3$)CH(CH_3)Ph), 1.49 (d, *J* = 6.7 Hz, 3H, NHCH(C<u>H</u>$_3$)Ph). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 164.6 (C, C-7a), 148.2 (CH, C-2), 145.8 (C, C$_{ipso}$), 137.1 (C, C-4a), 133.0 (CH, C-4), 128.4 (2CH, 2 × C$_{meta}$), 127.8 (2CH, 2 × C$_{ortho}$), 126.9 (CH, C$_{para}$), 121.8 (CH, C-3), 65.2 (CH, C-7), 63.0 (CH, N(CH_3)<u>C</u>H(CH_3)Ph), 33.3 (CH_3, N(<u>C</u>H$_3$)CH(CH_3)Ph) 28.3 (CH_2, C-6), 24.3 (CH_2, C-5), 21.3 (CH_3, N(CH_3)CH(<u>C</u>H$_3$)Ph). ESI-MS: calculated for $[C_{17}H_{21}N_2]^+$, 253.17; obtained, 253.15. $\alpha_D^{20\,℃} = +26.2$ (*c*1, $CHCl_3$).

*2.2.1.4. (S,S)-N-methyl-N-(1-phenylethyl)-6,7-dihydro-5H-cyclopenta[b]pyridin-7-amine [(S,S)-py$C_5H_5N(CH_3)CH(CH_3)Ph$)=**L2**]*

Following the general protocol for reductive amination, amine **5** (0.700 g, 2.94 mmol) was reacted with an aqueous 37% solution of formaldehyde (0.33 g, 4.4 mmol) and $NaBH(OAc)_3$ (1.869 g, 8.82 mmol). After the work-up procedure and purification, amine **L2** was obtained as a brown oil (0.549 g, 74%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.52–8.46 (m, 1H, H-2), 7.55–7.48 (m, 2H, ArH), 7.45 (dd, J = 7.6, 1.2 Hz, 1H, ArH), 7.35–7.28 (m, 2H, ArH), 7.26–7.20 (m, 1H, ArH), 7.05 (dd, J = 7.5, 4.9 Hz, 1H, H-3), 4.57 (t, J = 7.7 Hz, 1H, H-7), 4.16 (br s, 1H, N(CH_3)C<u>H</u>(CH_3)Ph), 2.88 (ddd, J = 16.1, 8.8, 4.7 Hz, 1H, H-5$_{syn}$), 2.74 (ddd, J = 16.3, 8.1, 7.7 Hz, 1H, H-5$_{anti}$), 2.15–1.97 (m, 5H, H-6$_{syn}$ + H-6$_{anti}$ + N(C<u>H</u>$_3$)CH(CH_3)Ph), 1.49 (d, J = 6.7 Hz, 3H, NHCH(C<u>H</u>$_3$)Ph). ^{13}C-NMR ($CDCl_3$, 101 MHz): δ = 164.2 (C, C-7a), 148.2 (CH, C-2), 145.9 (C, C$_{ipso}$), 137.1 (C, C-4a), 132.5 (CH, C-4), 128.4 (2CH, 2 × C$_{meta}$), 127.9 (2CH, 2 × C$_{ortho}$), 126.9 (CH, C$_{para}$), 121.9 (CH, C-3), 65.2 (CH, C-7), 63.0 (CH, N(CH_3)<u>C</u>H(CH_3)Ph), 33.4 (CH_3, N(<u>C</u>H$_3$)CH(CH_3)Ph), 28.3 (CH_2, C-6), 24.3 (CH_2, C-5), 21.3 (CH_3, N(CH_3)CH(<u>C</u>H$_3$)Ph). ESI-MS: calculated for $[C_{17}H_{21}N_2]^+$, 253.17; obtained, 253.19. $\alpha_D^{20\,°C} = -27.3$ (c1, $CHCl_3$).

2.2.2. General procedure for synthesis of tetracarbonyl complexes

In a Schlenk tube, $Mo(CO)_6$ and organic ligand **L1** or **L2** were reacted in refluxing anhydrous CH_3CN (40 mL) for 30 min under nitrogen. Solvent was removed from the resultant brown mixture by evaporation under reduced pressure, giving a brown solid that was washed with hexane (2 × 40 mL) and pentane (20 mL), and finally vacuum-dried.

*2.2.2.1. cis-[Mo(CO)$_4$(**L1**)] (**1**)*

$Mo(CO)_6$ (0.31 g, 1.17 mmol) was reacted with **L1** (0.30 g, 1.19 mmol), giving **1** in 54% yield (0.29 g). Anal. Calcd for $C_{21}H_{20}N_2MoO_4$ (460.33): C, 54.79; H, 4.38; N, 6.08. Found: C, 54.40; H, 4.45; N, 6.10%. Selected FT-IR (KBr, cm^{-1}): 359 (m), 705 (m), 796 (m), 944 (m), 1455 (m), 1822 (vs), 1868 (vs), 1892 (s), 2013 (s), 2854 (w), 2927 (m). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.58 (d, 1H, H-2), 7.6–7.2 (overlapping signals and multiplets, 6H, aryl-H and H-4), 7.14 (dd, 1H, H-3), 4.71 (t, 1H, H-7), 4.48 (q, 1H, N(CH_3)C<u>H</u>(CH_3)Ph), 2.93-2.63 (overlapping multiplets, 2H, H-5$_{syn}$ and H-5$_{anti}$), 2.6-2.0 (m, 5H, H-6$_{syn}$ + H-6$_{anti}$ + N(C<u>H</u>$_3$)CH(CH_3)Ph), 1.95 (d, 3H, N(CH_3)CH(C<u>H</u>$_3$)Ph).

*2.2.2.2. cis-[Mo(CO)$_4$(**L2**)] (**2**)*

$Mo(CO)_6$ (0.27 g, 1.02 mmol) was reacted with **L2** (0.26 g, 1.03 mmol), giving **2** in 64% yield (0.29 g). Anal. Calcd for $C_{21}H_{20}N_2MoO_4$ (460.33): C, 54.79; H, 4.38; N, 6.08. Found: C, 54.57; H, 4.79; N, 6.13%. Selected FT-IR (KBr, cm^{-1}): 363 (m), 705 (m), 795 (m), 944 (m), 1454 (m), 1822 (vs), 1868 (vs), 1893 (s), 2013 (s), 2857 (w), 2927 (m). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.58 (d, 1H, H-2), 7.6–7.2 (overlapping signals and multiplets, 6H, aryl-H and H-4), 7.14 (dd, 1H, H-3), 4.71 (t, 1H, H-7), 4.48 (q, 1H, $N(CH_3)C\underline{H}(CH_3)Ph$), 2.93-2.63 (overlapping multiplets, 2H, H-5$_{syn}$ and H-5$_{anti}$), 2.6-2.0 (m, 5H, H-6$_{syn}$ + H-6$_{anti}$ + $N(C\underline{H}_3)CH(CH_3)Ph$), 1.95 (d, 3H, $N(CH_3)CH(C\underline{H}_3)Ph$).

2.3. Catalytic tests

The catalytic reactions were carried out at 55 ºC under autogenous pressure in 10 mL borosilicate reactors possessing a Teflon valve for sampling, under magnetic stirring (1000 rpm). The reactor containing the catalyst (18 μmol), substrate (1.8 mmol) and 2 mL of co-solvent was immersed in a thermostated oil bath (under stirring) and, after 10 min, 2.75 mmol of oxidant (also pre-heated) was added (corresponding to the initial instant of the reaction). *cis*-Cyclooctene (Cy), DL-limonene (DL-Lim), *trans*-β-methylstyrene (*t*bms) were the substrates; 1,2-dichloroethane (DCE) and α,α,α-trifluorotoluene (TFT) were used as co-solvents (other than the decane present in the oxidant solution) for reactions of Cy and DL-Lim/*t*bms, respectively.

The reactions were monitored by analysis of samples taken at different reaction times using a Varian 3900 GC equipped with a flame ionization detector and a capillary column (J&W Scientific DB-5, 30 m × 0.25 mm × 0.25 μm). Undecane was used as internal standard (experimental range of error of less than 5%). The reaction products were identified by GC-MS (Trace GC 2000 Series Thermo Quest CE Instruments GC; Thermo Scientific DSQ II) using He as the carrier gas.

A biphasic solid/liquid reaction mixture was obtained for all systems after 24 h and, with the objective of identifying the active species, the liquid phase was separated from the solid phase by centrifugation (3000 rpm). The solids were thoroughly washed with diethyl ether (3 × 10 mL) and pentane (2 × 10 mL), dried at ambient temperature overnight, and finally vacuum-dried (ca. 0.1 bar) at 60 ºC for 1 h. These recovered solids are denoted as **i**-sub-run1, where **i** = **1** or **2**, and sub = Cy, DL-Lim or *t*bms.

The recovered solids **1**-Cy-run1 and **2**-Cy-run1 were tested for Cy reaction using the same mass ratio of molybdenum compound:olefin:oxidant as that used for the typical reaction conditions; after a 24 h batch run, the corresponding solids were recovered (denoted **1**-Cy-run2 and **2**-Cy-run2) using the same procedure described above for the original compounds.

3. Results and discussion

3.1. Catalyst preparation

Ligands **L1** and **L2** were prepared from ketone **3** (Scheme 1), which was obtained from 2,3-cyclopentenepyridine using an optimized protocol previously developed by some of us [20-22]. The reductive amination of ketone **3** with (*R*)-(+)-α-methylbenzylamine [(*R*)-PEA] and (*S*)-(−)-α-methylbenzylamine [(*S*)-PEA] using $NaBH(OAc)_3$ (STAB) as reducing agent proceeded diastereoselectively, affording **4-(*R*,*R*)** and **5-(*S*,*S*)**, respectively, as major diastereopure amines in good yields (80-84%). The subsequent *N*-methylation of the secondary amines **4** and **5** under the same protocol was accomplished using an aqueous solution of formaldehyde, yielding the title tertiary amines, **L1** and **L2** (74-78%).

The tetracarbonyl complexes *cis*-[$Mo(CO)_4$(**L1**)] (**1**) and *cis*-[$Mo(CO)_4$(**L2**)] (**2**) were obtained as brown solids in fair yields by reacting $Mo(CO)_6$ directly with the respective organic ligand **L1** or **L2** in refluxing CH_3CN. Complexes **1** and **2** display long-term stability in the solid-state if stored under inert atmosphere. However, in solution (the complexes are soluble in ethanol, acetone, diethyl ether, acetonitrile, toluene, ethyl acetate, chloroform and dichloromethane), the complexes present limited stability, being susceptible to decarbonylation reactions. Both complexes are insoluble in hexane, pentane and water. IR spectra of **1** and **2** in the solid-state (KBr pellets) display four CO stretching bands in the region 1810-2020 cm^{-1} in a pattern consistent with a *cis*-tetracarbonyl geometry. The solution ^1H NMR spectra confirm the presence of the organic ligands **L1** and **L2** and furthermore display peak shifts that can be attributed to coordination of the ligands to the metal center. For example, the resonances for the pyridyl ring protons H-2 and H-3 shift downfield from 8.5 and 7.05 ppm for the free ligands to 8.58 and 7.14 ppm for complexes **1** and **2** ($CDCl_3$ solvent). Similarly, the resonances for the methyne protons at 4.58 (H-7) and 4.16 ppm ($N(CH_3)C\underline{H}(CH_3)Ph$) for the free ligands shift to 4.71 and 4.48 ppm for the complexes.

3.2. Catalysis

3.2.1. General considerations using cis-cyclooctene as model substrate

Complexes **1** and **2** promoted the epoxidation of *cis*-cyclooctene (Cy) with TBHP at 55 ºC (DCE as cosolvent), and 1,2-epoxycyclooctane (CyO) was the only product formed (100% selectivity) (Fig. 2). Without molybdenum species and/or TBHP, olefin conversion was negligible, and thus metal species and the oxidant are required for the formation of active species. There is consensus across previously reported mechanistic studies that the active oxidizing species involves the coordination of the oxidant to the metal center [23-29]. The kinetic curves for **1** and **2** are roughly coincident, suggesting that the two compounds possess similar catalytic activity and stability, despite the chiral differences. High conversions were reached at 6 h (92-94%), and the reaction was complete within 24 h.

A comparison of the catalytic results for **1** and **2** with literature data (based on epoxide yields at 6 h, where CyO selectivity was always 100%) for neutral or ionic molybdenum tetracarbonyl compounds bearing pyridine-containing ligands (L), under somewhat comparable reaction conditions, indicates that the performances of **1** and **2** are far superior to the complexes with L = 2,2'-bipy (71% CyO yield) [15], di-*t*Bu-bipy (84%) [15], pypzH (51%) [16], or ethyl[3-(2-pyridyl)-1-pyrazolyl]acetate (70%) [16] (Table 1). N-heterocyclic carbene (NHC) complexes of the type $[Mo(CO)_4(NHC)_n]$ (NHC = 1,3-dibenzylimidazol-2-ylidene or 1,3-dipropylimidazol-2-ylidene (n = 2), or 3-methyl-1-picolylimidazol-2-ylidene (n = 1)) led to poorer catalytic results (ca. 9-35% CyO yield at 24 h, 55 ºC; Table 1) [30]. At the higher reaction temperature of 70 ºC, the complex $[Mo(CO)_4L]$ with L = *N*-[3-(trimethoxysilyl)propyl]ethylenediamine led to 47% CyO yield at 50% conversion, at 24 h (catalyst:olefin:oxidant = 1:159:317, mesitylene as cosolvent), which is much poorer than that for **1** and **2** [31].

The catalytic results for **1** and **2** are on a par with some of the best results reported in the literature for complexes of the type $[Mo(CO)_4L]$ tested as precatalysts for Cy reaction, at 55 ºC, specifically with L = 2-(1-pentyl-3-pyrazolyl)pyridine (93% CyO yield at 6 h) [19] and *N*-(*n*-propyl)-2-pyridylmethanimine (100% CyO yield at 5 h) [17].

3.2.2. Epoxidation of prochiral olefins

Compounds **1** and **2** were further explored for the epoxidation of prochiral olefins, namely *trans*-β-methylstyrene (*t*bms) and DL-limonene (DL-Lim) with TBHP at 55 ºC (TFT as cosolvent) (Fig. 2 and 3). With *t*bms as substrate, complexes **1** and **2** led to similar catalytic results (62%/85% and 59%/82% conversion at 6 h/24 h, for **1** and **2**, respectively), which

parallels that observed with Cy as substrate. The catalytic reaction of *t*bms was 100% selective towards the epoxide isomers (2*S*,3*S*)-2-methyl-3-phenyloxirane and (2*R*,3*R*)-2-methyl-3-phenyloxirane, which were formed in approximately equimolar amounts (enantiomeric excess (*ee*) was always ≤ 1%). Hence, asymmetric induction was negligible.

Poor asymmetric induction ability was reported for several molybdenum carbonyl complexes (with *t*bms as substrate), excluding chiral molybdenum tetracarbonyl complexes, which, to the best of our knowledge, have not been previously explored in catalytic olefin epoxidation [32-36]. This feature may be partly due to partial ligand dissociation and/or the pronounced distance between the olefin molecule and the chiral centers of the active oxidizing species (negligible stereochemical constraints for chiral induction ability), and/or involvement of radicals in the epoxidation reactions [33-36]. The catalytic results for **1** and **2** with *t*bms as substrate are comparable with results published for the chiral complex [(—)-menthylCp]Mo(CO)$_3$Cl (84% epoxide yield; 24 h, 55 ºC, $CHCl_3$) [32], molybdenum carbonyl complexes with *ansa*-bridged η^5-cyclopentadienyl ligands where the stereogenic centers are located in side chains (50-66% yield; 4 h, 55 ºC, toluene) [33], and the complex [(*N*-benzyloxycarbonylprolyl)cyclopentadienyl]Mo(CO)$_3$Me (84% yield; 24 h, 57 ºC, $CHCl_3$) [34] (in all these studies, total epoxide selectivity = 100% and Mo:olefin:oxidant = 1:100:200). Among these studies the maximum *ee* reported was 19-20% for the *ansa*-bridged complexes (the enantiomer in excess was not specified) [33] and the methyl-derived complex, which favored formation of the (2*R*,3*R*)-2-methyl-3-phenyloxirane enantiomer [32]. Further comparisons of the *t*bms epoxidation results for **1** and **2** with literature data for other molybdenum carbonyl complexes are difficult due to the broad range of reaction conditions used. The best result reported for the complexes (*R*)-Cp^{ox}M(η^3-C_3H_5)(CO)$_2$ (M = Mo, W) and [(*R*)-Cp^{ox}Mo(CO)$_2$(NCMe)]BF_4 (Cp^{ox} = chiral oxazoline pendant group) was 58% conversion (100% epoxide selectivity) after 6 h reaction at ambient temperature (Mo:olefin:oxidant = 1:100:200, $CHCl_3$) [36]. The complexes CpMo(CO)$_3$X with X = CHR^{2}CO(OR^1) (R^1 = ethyl, menthyl or bornyl, R^2 = H; R^1 = ethyl, R^2 = methyl or phenyl) led to 62-70% epoxide yield (100% selectivity) after 8.3 h reaction at ambient temperature (Mo:olefin:oxidant = 1:100:200, CH_2Cl_2) [35]. The two latter works reported negligible *ee*'s.

Complexes **1** and **2** were further tested for the epoxidation of the bio-derived olefin DL-limonene (DL-Lim). Limonene is produced via distillation of crude turpentine, and is a valuable by-product of pine oil and camphor processes. Limonene epoxidation leads to valuable products, such as limonene-1,2-monoepoxide (limonene oxide, abbreviated as LO) and 1,2:8,9-diepoxy-*p*-menthane (limonene dioxide, abbreviated as LDO). The relative

abundance, low cost, and structural similarity to cyclohexene oxide, make LO an attractive choice as a biorenewable epoxide monomer for copolymerization with CO_2, giving a biodegradable polycarbonate (LDO may also be used) and, consequently, providing an attractive green route to non-isocyanate polyurethanes without requiring the use of either toxic isocyanate monomers or phosgene [37-39]. In the same way, LO can give polyesters by reaction with succinic anhydride [40]. LO/LDO can be used as intermediates for the manufacture of perfumes, flavors and fragrances, as green solvents, and as reactive diluents in cationic and UV cure applications [39,41-43]. Geoghegan and Evans employed LO as a starting material for the synthesis of (+)-perillyl alcohol [44], which may be useful as a "chiral pool" starting material and as an anti-cancer agent [45].

The reaction of (racemic) DL-Lim with TBHP, in the presence of **1** or **2** at 55 ºC, led to similar catalytic results, in parallel to that observed for the two complexes with Cy or *t*bms as substrates. The DL-Lim conversions were 85% and 96-97% at 6 h and 24 h, respectively (Fig. 3). The main reaction products were LO isomers, namely (1*S*,4*S*)-(−)-*cis*-limonene-1,2-epoxide and (1*R*,4*S*)-(−)-*trans*-limonene-1,2-epoxide (diastereomers formed from (*S*)-(−)-limonene (S-Lim)), and (1*S*,4*R*)-(+)-*cis*-limonene-1,2-epoxide and (1*R*,4*R*)-(+)-*trans*-limonene-1,2-epoxide (diastereomers formed from (*R*)-(+)-limonene (R-Lim)), which were formed with total (LO) selectivity of 80-82% and 69-70%, at 6 h and 24 h, respectively (Scheme 2).

Slight enantiomeric excesses (*ee's)* of the (+) LO isomers were obtained at 24 h (ca. 4% of isomer II relative to III and 14-16% of isomer I relative to III). On the other hand, slight diastereomeric excess (*de*) of *trans* limonene-1,2-epoxide isomers was obtained at 24 h (3-4% of isomer I relative to II and 6-9% of isomer III relative to IV).

Other products of the DL-Lim reaction included LDO (selectivities of 12-13% at 6 h and 19-20% at 24 h) and 1-methyl-4-(1-methylethenyl)-cyclohexane-1,2-diol (LDOH; selectivities of 0-2% at 6 h and 8-9% at 24 h). The ratio LO/(LO+LDO) was in the range 0.8-1, indicating high chemoselectivity in favor of the epoxidation of the endocyclic double bond. LO selectivity decreased with time, and LDO selectivity increased (Fig. 3). On the other hand, 8,9-epoxy-*p*-menth-1-ene was not formed, suggesting that LDO is formed via consecutive epoxidation of LO.

To the best of our knowledge, there are no reports on the use of chiral molybdenum carbonyl complexes as precatalysts for the reaction of racemic DL-Lim, although it was reported that they may promote the reaction of the pure isomers of limonene with TBHP. Specifically, the complex $[Mo(CO)_3I_2$(4,4'-dimethyl-2,2'-bipyridine)] led to 56% conversion

of *R*-(+)-Lim and 91% selectivity to the monoepoxides (1*S*,4*R*)-(+)-*cis*- (II) and (1*R*,4*R*)-(+)-*trans*-limonene-1,2-epoxide (I), and *de* was less than 5% (24 h, 55 ºC, Mo:olefin:oxidant = 1:100:200, CH_2Cl_2) [46]. The complexes (*R*)-$Cp^{ox}M(\eta^3\text{-}C_3H_5)(CO)_2$ (M = Mo, W) and [(*R*)-$Cp^{ox}Mo(CO)_2(NCMe)]BF_4$ led to quantitative conversion of *R*-(+)-Lim to LO after 1 h reaction at 55 ºC [36]; an approximately equimolar mixture of LO isomers was obtained for the neutral complex, while 20% *de* of the (+)-*cis* isomer was obtained for the cationic complex (Mo:olefin:oxidant = 1:100:200, $CHCl_3$).

The few published studies that report the Mo-catalyzed reaction of DL-Lim with TBHP use chiral oxomolybdenum compounds as (pre)catalysts (Table 2). In general, compounds **1** and **2** studied in this work led to comparable results (in terms of LO yields at 24 h) to those obtained with the polymeric compound $[((Me)_2(menthyl)Sn)_2MoO_4(H_2O)_{3.5}]$ [47], and slightly better results than those for the complex $[MoO_2\{(-)\text{-}2,2\text{-bis}[(4S,5S)\text{-}4\text{-hydroxymethyl-5-phenyl-1,3-oxazolin-2-yl}]\text{propane}\}]$ [48]. The hybrid polymer $[Mo_2O_6(trethbz)_2]\cdot H_2O$ (*trethbz* = (*S*)-4-(1-phenylpropyl)-1,2,4-triazole) led to higher yields (82%) [49]. The (+)-*cis* and (+)-*trans* LO isomers were predominantly formed relative to (−)-*cis* and (−)-*trans*, respectively, using all Mo compounds, with the best *ee*'s observed for **1** and **2** and also $[Mo_2O_6(trethbz)_2]\cdot H_2O$ as (pre)catalysts. The dioxomolybdenum(VI) complex containing the chiral oxazoline ligand led to the highest *de* (18-20% of *trans* isomers) [48].

3.2.3 Nature of active species

Complexes **1** and **2** are converted into active oxidizing species (discussed above) *in situ* during the catalytic process. Structural modification of the starting complexes is somewhat supported by the fact that the color of the Cy reaction mixtures containing (**1** or **2**)/olefin/TBHP changed from greenish to light brown upon addition of the oxidant to the reactor. The metal species were isolated after a 24 h batch run, giving the solids **1**-Cy-run1 and **2**-Cy-run1, and characterized by ATR FT-IR spectroscopy (Fig. 4). Indicators for oxidative decarbonylation of the precatalysts are the disappearance of the CO stretching bands in the region 1810-2020 cm^{-1} and the appearance of several new bands in the Mo–O stretching region of 650-950 cm^{-1}. Similar spectra were obtained for the solids isolated after catalytic reactions with the other substrates (Fig. 4). The pattern of bands in the Mo–O stretching region is highly characteristic of the β-octamolybdate anion, β-$[Mo_8O_{26}]^{4-}$, as supported by the literature data given in Table 3 for comparison. This polyoxomolybdate had previously been identified as the product of oxidative decarbonylation of the complexes

$[Mo(CO)_3I_2L_2]$ (L = pyridine or 4-*tert*-butylpyridine), which gave the salts $(LH)_4[Mo_8O_{26}]$ [50]. The Cy/TBHP reaction in the presence of **1**-Cy-run1 or **2**-Cy-run1 led to similar catalytic results to the respective parent compounds **1** and **2** (Fig. 2). Compounds **1**-Cy-run2 and **2**-Cy-run2 exhibited similar ATR FT-IR spectra to **1**-Cy-run1 and **2**-Cy-run1, suggesting that the polynuclear species formed is chemically stable during the catalytic reaction (Fig. 4). On the other hand, these results suggest that the active species formed from the precursors **1** and **2** are responsible for the catalytic epoxidation process in the first and second batch runs.

4. Conclusions

The efficacy of molybdenum carbonyl complexes as precatalysts for olefin epoxidation reactions has motivated some efforts to prepare chiral catalyst precursors in the hope that these may promote asymmetric induction. In the present work we have described the first report of the application of chiral molybdenum tetracarbonyl complexes in catalytic olefin epoxidation. Although epoxides were either the main or only products formed from *cis*-cyclooctene, *trans*-β-methylstyrene and DL-limonene, stereoselectivities were low with the prochiral olefins. The lack of success in asymmetric epoxidation may be partly due to the labile behavior of the 7-(1-pyrindanyl) amine ligands, which decoordinate upon oxidative decarbonylation of the precursors to give β-octamolybdate salts in which the protonated organic ligand is present as charge-balancing cation. Our previous work with *cis*-$[Mo(CO)_4(L)]$ catalyst precursors has indicated that chelating ligands such as bipyridines and pyrazolylpyridines tend to remain coordinated to the metal center upon oxidative decarbonylation to give either discrete polynuclear oxo-complexes or hybrid molybdenum oxide/organic polymers, and therefore better success in asymmetric epoxidation may be achieved by employing chiral derivatives of these types of ligands.

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Figure captions

Scheme 1. Preparation of the ligands (**L1** and **L2**) and corresponding tetracarbonyl complexes (**1** and **2**).

Scheme 2. Products formed from DL-limonene epoxidation.

Fig. 1. Atom labelling used in the NMR peak assignments.

Fig. 2. Kinetic profiles for the catalytic reactions **1**/Cy (Δ), **2**/Cy (○), **1**-Cy-run1/Cy (+), **2**-Cy-run1/Cy (-), **1**/*t*bms (◊) and **2**/*t*bms (□), using TBHP as oxidant at 55 ºC.

Fig. 3. Kinetic profile of the reaction of DL-Lim with TBHP, in the presence of **1** (+) or **2** (×), at 55 ºC, and selectivity to the products LO (▲,Δ), LDO (●,○) and LDOL (■,□) for reactions of **1** (closed symbols) or **2** (open symbols).

Fig. 4. FT-IR spectra in the range 500-2100 cm^{-1} of **L1** and complex **1**, and ATR FT-IR spectra of solids recovered after catalytic reactions.

Table 1

cis-Cyclooctene epoxidation at 55 ºC in the presence of compounds **1** and **2**, and comparison with literature data for molybdenum tetracarbonyl complexes.

Complex[a]	Reaction conditions			Conv.[c] (%)	Select. (%)[d]	Ref.
	Mo:Cy:TBHP	Cosolvent[b]	*t* (h)			
1	1:100:153	DCE	6/24	92/100	100/100	This work
2	1:100:153	DCE	6/24	94/100	100/100	This work
$[Mo(CO)_4$(2,2'-bipy)]	1:100:153	DCE	6	71	100	[15]
$[Mo(CO)_4$(di-*t*Bu-bipy)]	1:100:153	DCE	6	84	100	[15]
$[Mo(CO)_4$(pzpyH)]	1:100:152	None	6/24	51/78	100/100	[16]
$[Mo(CO)_4$(pzpyE)]	1:100:152	None	6/24	70/92	100/100	[16]
$[Mo(CO)_4$(pzpyP)]	1:113:172	DCE	6/24	93/100	100/100	[19]
$[Mo(CO)_4$(pyim)]	1:100:153	None	5	100	100	[17]
$[Mo(CO)_4(IBz)_2]$	1:100:200	None	4/24 h	~7/~35	100/100	[30]
$[Mo(CO)_4(IPr)_2]$	1:100:200	None	4/24 h	~10/~32	100/100	[30]
$[Mo(CO)_4$(PyNHC)]	1:100:200	None	4/24 h	~2/~9	100/100	[30]

[a] 2,2'-bipy = 2,2'-bipyridine, di-*t*Bu-bipy = 4,4'-di-*tert*-butyl-2,2'-bipyridine, pzpyH = 2-[3(5)-pyrazolyl]pyridine, pzpyE = ethyl[3-(2-pyridyl)-1-pyrazolyl]acetate, pzpyP = 2-(1-pentyl-3-pyrazolyl)pyridine, pyim = *N*-(*n*-propyl)-2-pyridylmethanimine, IBz = 1,3-dibenzylimidazol-2-ylidene, IPr = 1,3-dipropylimidazol-2-ylidene, PyNHC = 3-methyl-1-picolylimidazol-2-ylidene.

[b] Other than decane from oxidant solution.

[c] *cis*-Cyclooctene conversion.

[d] Selectivity to the epoxide (CyO).

Table 2

Limonene epoxidation with TBHP and chiral Mo compounds at 55 ºC.

Compound[a]	Sub.[b]	Mo:Sub:TBHP	Solv.[c]	C (%)[d]	Y (%)[e]	*ee* (%)[f]	*de* (%)[g]	Ref.
1	DL-Lim	1:100:153	TFT	96	67	4 (II)	6 (III)	This work
						14 (I)	3 (I)	
2	DL-Lim	1:100:153	TFT	97	68	4 (II)	9 (III)	This work
						16 (I)	4 (I)	
$[(Me_2RSn)_2MoO_4(H_2O)_{3.5}]$	DL-Lim	1:100:150	CH_2Cl_2	90	65-67	-	-	[47]
	R-Lim			85		-	5 [h]	
	S-Lim			97		-	5 [h]	
$[Mo_2O_6(trethbz)_2]\cdot H_2O$	DL-Lim	1:100:153	TFT	90	82	12 (II)	3 (IV)	[49]
						18 (I)	8 (II)	
$[MoO_2(oxazol)]$	DL-Lim	1:138:211	DCE	90	59	13 (III)	18 (I)	
						25 (I)	20 (III)	
	R-Lim			87	68	-	22 (I)	[48]
	S-Lim			88	60	-	19(III)	

[a] R = menthyl; *trethbz* = (*S*)-4-(1-phenylpropyl)-1,2,4-triazole; oxazol = (−)-2,2-bis[(4*S*,5*S*)-4-hydroxymethyl-5-phenyl-1,3-oxazolin-2-yl]propane.

[b] Substrates: DL-Lim = DL-limonene; *R*-Lim = *R*-(+)-limonene; *S*-Lim = *S*-(−)-limonene.

[c] Solv. = cosolvent added (other than decane from oxidant solution).

[d] Conversion of the substrate after 24 h.

[e] Total yield of 1,2-epoxides after 24 h.

[f] Enantiomeric excess at 24 h; the isomer in excess is indicated within brackets (pairs of enantiomers I/III and II/IV).

[g] Diastereomeric excess at 24 h; the isomer in excess is indicated within brackets (pairs of diastereomers I/II and III/IV).

[h] The isomer in excess was not specified.

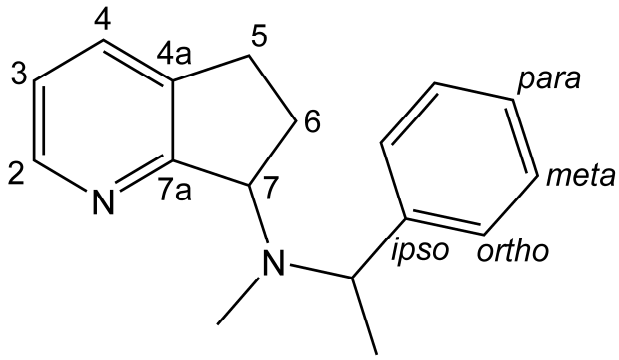
Table 3

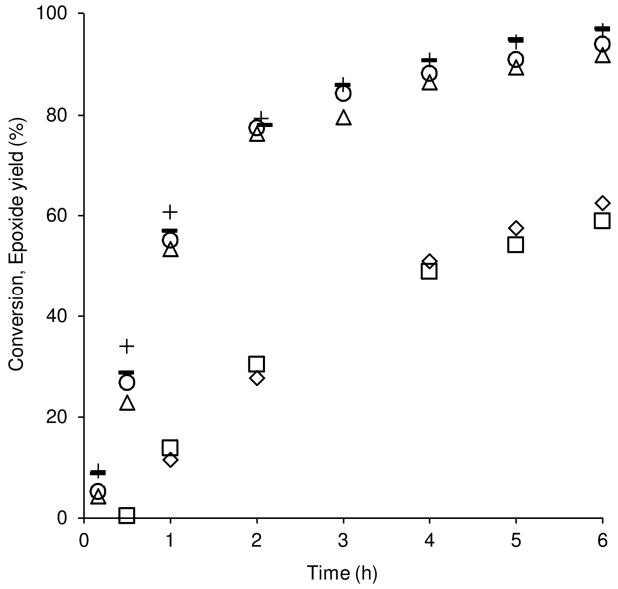
Comparison of infrared bands observed for the recovered compounds **1**-Cy-run1 and **2**-Cy-run1 in the range 650-950 cm^{-1} with bands exhibited by *β*-octamolybdate salts.

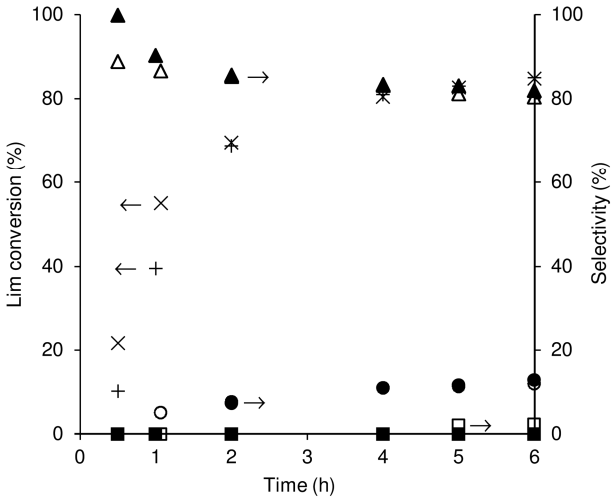
Compound[a]	IR bands (cm^{-1})					Ref.
1-Cy-run1, **2**-Cy-run1[b]	942	903	844	701	659	This work
$(pyH)_4[Mo_8O_{26}]$	946	912	839	709	675	[50]
$(t\text{BupyH})_4[Mo_8O_{26}]$	949	914	837	708	659	[50]
$(H_3biim)_4[Mo_8O_{26}]$	944	919	838	686	670	[51]
$(HDBU)_3(NH_4)[Mo_8O_{26}]\cdot H_2O$	939	910	842	720	669	[52]
$(Hmim)_4[Mo_8O_{26}]$	946	910	841	710	665	[53]
$(Dhmim)_4[Mo_8O_{26}]$	956	911	837	714	650	[53]
$(Hpy)_4[Mo_8O_{26}]\cdot H_2O$	947	911	836	717	632	[53]
$(Bmim)_4[Mo_8O_{26}]$	939	913	842	714	661	[54]
$(dmimX)_3[Mo_8O_{26}]_2(H_3O)_2\cdot H_2O$	944	902	841	711	651	[55]
$(4,4'\text{-}H_y bipy)_{4/y}[Mo_8O_{26}]$[b]	935	910	836	699,	657	[56]

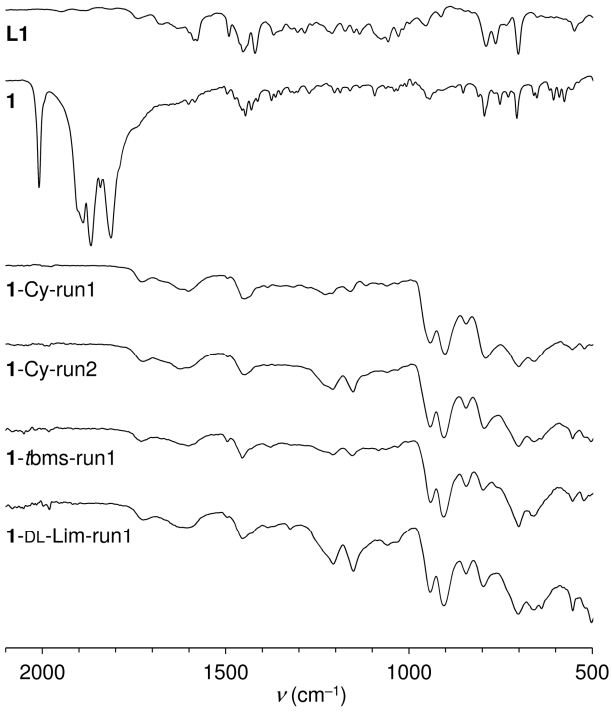
[a] pyH = pyridinium; *t*BupyH = 4-*tert*-butylpyridinium; H_2biim = 2,2'-biimidazole; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; Hmim = 1-hexyl-3-methylimidazolium; Dhmim = 1,2-dimethyl-3-hexylimidazolium; Hpy = 1-hexylpyridinium; Bmim = 1-butyl-3-methylimidazolium; dmimX = bis(1,2-dimethylimidazolium) p-xylenedichloride; 4,4'-bipy = 4,4'-bipyridine.

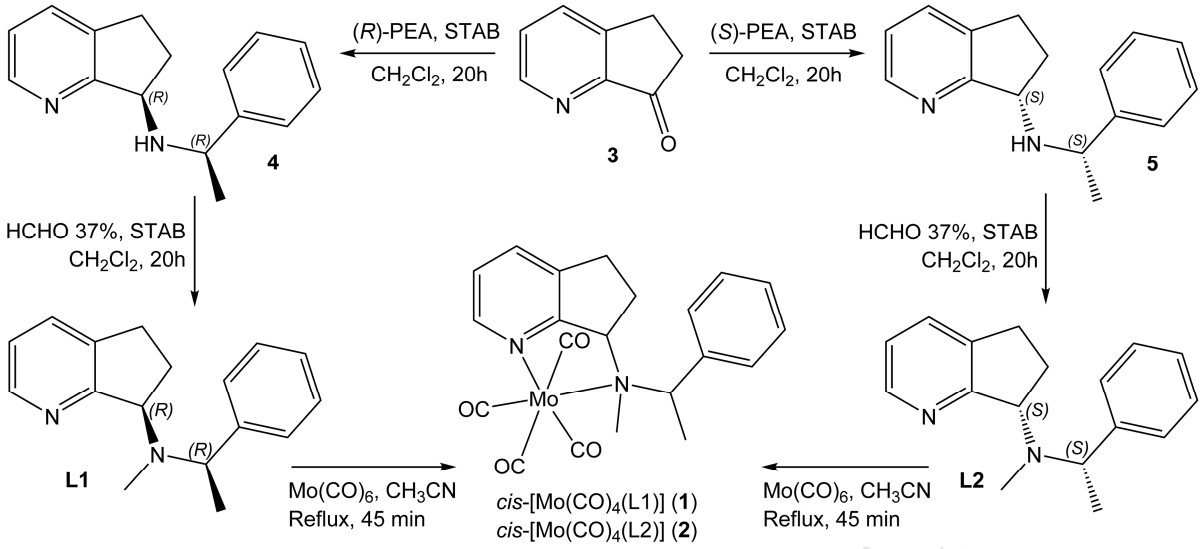
[b] ATR FT-IR bands.

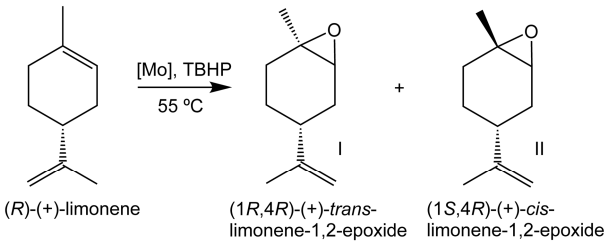








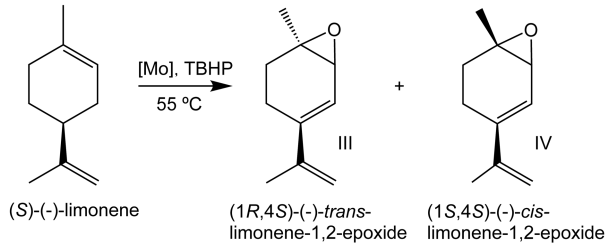




(*R*)-(+)-limonene

(1*R*,4*R*)-(+)-*trans*-limonene-1,2-epoxide

(1*S*,4*R*)-(+)-*cis*-limonene-1,2-epoxide



(*S*)-(-)-limonene

(1*R*,4*S*)-(-)-*trans*-limonene-1,2-epoxide

(1*S*,4*S*)-(-)-*cis*-limonene-1,2-epoxide

1) Two chiral tetracarbonylmolybdenum pyrindanyl amine complexes have been synthesized.

2) The tetracarbonyls can be used catalyst precursors for olefin epoxidation with TBHP.

3) Epoxides were obtained as the main/only products from achiral/prochiral olefins.

4) Oxidative decarbonylation of the precursors with TBHP gives β-octamolybdate salts.