Molybdenum(VI) oxides bearing 1,4,7-triazacyclononane and 1,1,1-tris(aminomethyl)ethane ligands: Synthesis and catalytic applications

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Abstract

A series of ionic dioxomolybdenum(VI) complexes of general formula $[MoO_2Cl(L)]Y$ containing tridentate nitrogen ligands [L = 1,4,7-triazacyclononane (tacn), 1,1,1-tris(methylaminomethyl)ethane (Me_3-tame) and N,N',N''-tribenzyl-1,1,1-tris(methylaminomethyl)ethane (Bn_3Me_3-tame); Y = Cl, BF_4^-] were prepared by replacement of the solvent molecules and one of the chloride ligands in the adducts $MoO_2Cl_2(solv)_2$ (solv = THF, DMF). The complexes were examined as catalysts for the epoxidation of cyclooctene at 55 °C, using *tert*-butyl hydroperoxide (*t*-BuOOH) as the oxidant. The kinetic profiles and initial activities (60–100 mol mol_{Mo}^{-1} h^{-1}) were comparable with those usually exhibited by MoO_2Cl_2L complexes bearing bidentate heterocyclic amines. The tricarbonyl complexes (Me_3-tame)M(CO)$_3$ (M = Mo, Cr) were also prepared and used directly as catalyst precursors for the epoxidation of cyclooctene using *t*-BuOOH. Induction periods were observed due to relatively slow oxidative decarbonylation and formation of the active oxidising species. When the Mo tricarbonyl complex was used, 1,2-epoxycyclooctane was the only product, while with the Cr complex a significant amount of 1,2-cyclooctanediol was formed due to the enhanced Lewis acidity of the active catalyst. The Mo complexes containing the tame ligands were further studied as catalysts or catalyst precursors for the epoxidation of cyclododecene, 1-octene, *trans*-2-octene, (R)-(+)-limonene and α-pinene.
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1. Introduction

Homogeneous molybdenum(VI) catalysts containing the *cis*-$[MoO_2]^{2+}$ unit are the basis of important industrial oxidation processes using alkyl hydroperoxides as the oxygen source [1,2]. As a result, a large number of dioxomolybdenum(VI) complexes of the type $MoO_2X_2(L')_n$ [3–19], $[MoO_2X(L')]Y$ [9,15], $MoO_2X(L'')_m(L')_n$ [9–11] and $MoO_2(L'')_m(L')_n$ [10,11,20] [X = Cl, Br, CH$_3$; L = mono-, bi- or tri-dentate neutral (L') or anionic (L'') N,O,S-ligand] have been studied as catalysts for the reaction of olefins with *t*-BuOOH. The complexes are nearly all six-coordinate and usually exhibit distorted octahe- dral geometry. Important properties, such as the solubility of the complex and the Lewis acidity of the metal centre, can be fine-tuned by variation of the first-sphere ligands. In the last few years, complexes of the type (η^5-C_5R_5)MoO$_2$Cl have also been shown to be promising catalysts for the epoxidation of olefins using *t*-BuOOH [21–25]. Turnover frequencies (TOF) of up to 21,000 mol mol_{Mo}^{-1} h^{-1} were obtained that even surpass that of the well-known CH$_3$ReO$_3$/H$_2$O$_2$ system. The (η^5-C_5R_5)chlorodioxomolybdenum(VI) complexes are easily prepared from their corresponding and readily available (η^5-C_5R_5)Mo(CO)$_3$Cl precursors by reaction with *t*-BuOOH in *n*-decane [21]. In fact, the parent tricarbonyl complexes can be applied directly as catalyst precursors in the olefin epoxidation, without isolation of the dioxo complexes prior to use [22,24].

Complexes of the type $[MoO_2X(L')]Y$ and $MoO_2X(L'')$ bearing tripodal ligands can be considered as being

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analogous to the (η^5-C$_5$R$_5$)chlorodioxomolybdenum(VI) complexes. In 1985, Wieghardt and co-workers reported the synthesis of [MoO$_2$Br(Me$_3$tacn)]Br$_3$ (Me$_3$tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane) by oxidative decarbonylation of [Mo(CO)$_3$Br(Me$_3$tacn)]Br [26]. Perchlorate or hexafluorophosphate salts of the dioxomolybdenum(VI) complex were also obtained [26], but these were not studied for their catalytic behaviour. More recently, it was found that reaction of MoO$_2$X$_2$(THF)$_2$ (X = Cl or Br) with tridentate ligands, namely *tris*(1-pyrazolyl)methane [HC(pz)$_3$] and *tris*(3,5-dimethyl-1-pyrazolyl)-methane [HC(3,5-Me$_2$pz)$_3$], leads to the replacement of both coordinated solvent molecules and one of the chloride ligands to give [MoO$_2$X(L$'$)]X [9]. The turnover frequencies of the complexes in olefin epoxidation, with *t*-BuOOH as the oxidising agent, were in the middle of the range observed for MoO$_2$X$_2$L$_2$ complexes with N-donor ligands (20–600 mol mol$_{Mo}^{-1}$ h^{-1}). In the present work, we describe the synthesis and characterisation of molybdenum(VI) oxocomplexes bearing triaza-ligands based on either 1,4,7-triazacyclononane (tacn) or 1,1,1-tris(aminomethyl)ethane (tame). The complexes (Me$_3$-tame)M(CO)$_3$ (M = Mo, Cr) were also synthesised for comparison purposes. All of the complexes were tested as (pre)catalysts for the epoxidation of cyclooctene using *t*-BuOOH 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, distilled under nitrogen and stored over molecular sieves. Microanalyses for C, H and N were carried out at the ITQB (by C. Almeida). IR spectra were obtained as KBr pellets using a FTIR Mattson-7000 infrared spectrophotometer. ^{1}H NMR spectra were recorded at 300 MHz using a Bruker CXP 300 spectrometer. The compounds *N,N$'$,N$''$*-tribenzyl-1,1,1-tris(methylaminomethyl)ethane (Bn$_3$Me$_3$-tame) [15], 1,1,1-tris(methylaminomethyl)ethane (Me$_3$-tame) [27], 1,4,7-triazacyclononane (tacn) [28], MoO$_2$Cl$_2$ [29,30], MoO$_2$Cl$_2$(DMF)$_2$ [30] and [MoO$_2$Cl(Bn$_3$Me$_3$-tame)]BF$_4$ (**3**) [15] were prepared as described in the literature. ^{1}H NMR data for Bn$_3$Me$_3$-tame (300 MHz, C$_6$D$_6$, r.t.): δ = 7.40–7.11 (m, 15H), 3.54 (s, 6H), 2.54 (s, 6H), 2.18 (s, 9H), 1.18 (s, 3H). ^{1}H NMR data for **3** (300 MHz, d_7-DMF, r.t.): δ = 7.55–7.44 (m, 15H), 4.18 (s, 6H), 3.49 (s, 2H), 3.23 (s, 4H), 2.7 (s, 9H), 1.48 (s, 3H).

2.2. [MoO$_2$Cl(tacn)]Cl (**1**)

A solution of MoO$_2$Cl$_2$(DMF)$_2$ (267 mg, 0.77 mmol) in acetonitrile (10 ml) was treated with tacn (100 mg, 0.77 mmol), and the mixture was stirred vigorously for 1 h at room temperature, resulting in the formation of a precipitate. The solid was filtered off, washed with acetonitrile and diethyl ether. Drying in vacuum gave compound **1** as a pink powder (225 mg, 61%). Found: C, 21.68; H, 4.86; N, 12.78%. C$_6$H$_{15}$N$_3$MoO$_2$Cl$_2$ (328.05) requires C, 21.97; H, 4.61; N, 12.81%. IR (KBr, cm^{-1}): 3442 w, 3062 w, 2969 w, 2848 w, 2770 w, 1454 m, 1274 m, 1232 m, 1107 m, 1077 m, 1060 m, 932 s, 908 s, 780 m.

2.3. [MoO$_2$Cl(Me$_3$-tame)]Cl (**2**)

2.3.1. Method (a)

A solution of MoO$_2$Cl$_2$(DMF)$_2$ (394 mg, 1.14 mmol) in acetonitrile (10 ml) was treated with a solution of Me$_3$-tame (200 mg, 1.26 mmol) in acetonitrile (2 ml) under nitrogen, and the mixture was stirred vigorously for 1 h at room temperature, resulting in the formation of a precipitate. The solid was filtered off and washed with acetonitrile. Drying in vacuum gave compound **2** as a colourless powder (363 mg, 89%).

2.3.2. Method (b)

A solution of Me$_3$-tame (108 mg, 0.68 mmol) in THF (7 ml) was added to a solution of MoO$_2$Cl$_2$(THF)$_2$ (213 mg, 0.62 mmol) in THF (7 ml). A precipitate formed immediately, and the reaction mixture was left to stir at room temperature. The solid was filtered off and washed with THF. Drying in vacuum gave compound **2** as a pink powder (211 mg, 95%). Found: C, 26.69; H, 6.60; N, 11.46%. C$_8$H$_{21}$N$_3$MoO$_2$Cl$_2$ (358.12) requires C, 26.83; H, 5.91; N, 11.73%. IR (KBr, cm^{-1}): 3460 w, 2974 w, 2718 w, 2414 m, 1656 m, 1587 m, 1463 s, 1157 m, 1103 m, 1029 m, 944 m, 905 s, 820 m, 707 m, 664 m.

2.4. (Me$_3$-tame)Mo(CO)$_3$ (**4**)

A mixture of Mo(CO)$_6$ (1.70 g, 6.46 mmol) and Me$_3$-tame (1.03 g, 6.46 mmol) in decaline (35 ml) was heated under nitrogen at 130 °C for 2 h. After cooling, the resultant solid was filtered off and washed with toluene. Drying in vacuum gave compound **4** as a yellow powder (1.58 g, 72%). Found: C, 38.79; H, 6.40; N, 12.35%. C$_{11}$H$_{21}$N$_3$MoO$_3$ (339.25) requires C, 38.95; H, 6.24; N, 12.39%. IR (KBr, cm^{-1}): 3309 s, 3273 s, 2999, 2967 m, 2919 m, 2866 m, 2820 w, 2805 w, 1892 vs, 1776 vs, 1721 vs, 1474 s, 1459 sh, 1396 m, 1261 m, 1178 m, 1065 m, 1033 s, 993 m, 973 m, 942 s, 920 s, 897 m, 875 m.

2.5. (Me$_3$-tame)Cr(CO)$_3$ (**5**)

A mixture of Cr(CO)$_6$ (553 mg, 2.51 mmol) and Me$_3$-tame (400 mg, 2.51 mmol) in decaline (15 ml) was heated under nitrogen at 130 °C for 24 h. After cooling, the resultant solid was filtered off and washed with toluene. Drying in vacuum gave compound **5** as a dark yellow powder (330 mg, 45%). Found: C, 44.30; H, 7.52; N, 14.08%. C$_{11}$H$_{21}$N$_3$CrO$_3$ (295.30) requires C, 44.73; H, 7.17; N, 14.24%. IR (KBr, cm^{-1}): 3440 w, 3315 m, 3286 m, 2979, 2967, 2890, 2873, 1890 vs, 1766 vs, 1738 vs, 1713 vs, 1642 m, 1475, 1075, 1034, 994, 976, 943, 921.

2.6. Catalysis

The liquid-phase catalytic epoxidations were carried out at 55 °C under air (atmospheric pressure) in a reaction vessel equipped with a magnetic stirrer and immersed in a thermostated

oil bath. A 1% molar ratio of complex/substrate and a substrate/oxidant molar ratio of 0.65 (TBHP, 5.5 M in decane) were used. The course of the reaction was monitored using a gas chromatograph (Varian 3800) equipped with a capillary column (SPB-5, 20 m × 0.25 mm) and a flame ionisation detector. The products were identified by gas chromatography–mass spectrometry (HP 5890 Series II GC; HP 5970 Series Mass Selective Detector) using He as carrier gas.

3. Results and discussion

3.1. Synthesis and characterisation

Treatment of the solvent adducts $MoO_2Cl_2(solv)_2$ (solv = THF, DMF) with the tripodal N-ligands tacn and Me_3-tame gave the ionic complexes $[MoO_2Cl(tacn)]Cl$ (**1**) and $[MoO_2Cl(Me_3$-tame)]Cl (**2**) (Scheme 1). The complex $[MoO_2Cl(Bn_3Me_3$-tame)]BF_4 (**3**) was synthesised as described previously by the reaction of $[MoO_2Cl(THF)_3]BF_4$ (formed in situ) with Bn_3Me_3-tame in THF [15]. In all cases the products precipitated from the reaction mixtures and were isolated in a pure form by filtration and washing with acetonitrile or THF, and diethyl ether. Compounds **1–3** are hygroscopic and moisture sensitive, and are only soluble in very polar solvents such as DMSO and DMF.

A ^{1}H NMR spectrum of acceptable quality was only obtained for compound **3** in d_7-DMF. As expected, the proton signals for **3** are shifted to lower field (by up to 1 ppm) with respect to the signals for the free ligand. The signal of the CH_2 group adjacent to the quaternary carbon atom splits into two singlets with a 2:1 relative intensity ratio, indicating that the C_{3v} symmetry of the ligand Bn_3Me_3-tame is lost upon coordination to the metal centre. The minor signal at δ 3.49 ppm is deshielded by almost 1 ppm with respect to the signal for the free ligand (δ 2.54 ppm). The benzylic methylene and methyl substituent groups on the nitrogen atoms have equal signals in ^{1}H NMR spectrum, pointing to a fast dissociation of the Mo–N bond(s) followed by an interchange of the positions of the methyl and benzyl groups, and then re-association of the Mo–N bonds. On the other hand, the dissociation-re-association of the Mo–N bond does not substantially affect the positions of the methylene groups adjacent to the quaternary carbon atom, and therefore they appear in the spectrum as two signals in a 2:1 ratio, pointing to the presence of pseudo C_s-symmetry (Fig. 1). The symmetry plane includes the chlorine and molybdenum atoms, the angular methyl group, the quaternary carbon atom, and the adjacent CH_2 group and nitrogen atom (designated as N' in Fig. 1) that belong to the ligand branch in trans position to the chlorine. It was expected that low temperature ^{1}H NMR experiments would provide additional splitting of the benzylic methylene and N-methyl signals, because of a slowed down isomerisation process. Indeed, a better-defined spectrum was obtained at 283 K, but a further decrease in the temperature provoked a broadening of the signals, probably because of an increase in the viscosity of the solution. For complexes **1–3**, no ^{13}C NMR spectra could be obtained due to the low solubility of the complexes in non-coordinating solvents, and their slow decomposition in d_6-DMSO and d_7-DMF.

The infrared spectra of compounds **1–3** exhibit two strong ν(Mo=O) bands at 930–950 and 905–915 cm^{-1}, assigned to the symmetric and asymmetric vibrations of the cis-$[MoO_2]^{2+}$ fragment, respectively. The values are 932 and 908 cm^{-1} for $[MoO_2Cl(tacn)]Cl$ (**1**), 944 and 905 cm^{-1} for $[MoO_2Cl(Me_3$-tame)]Cl (**2**), and 948 and 913 cm^{-1} for $[MoO_2Cl(Bn_3Me_3$-tame)]BF_4 (**3**). The stretching frequencies for **3** are significantly higher than those for **2**, indicating a stronger metal–oxygen interaction. This may be related with the increased steric bulk of the Bn_3Me_3-tame ligand, which may hinder the approach of
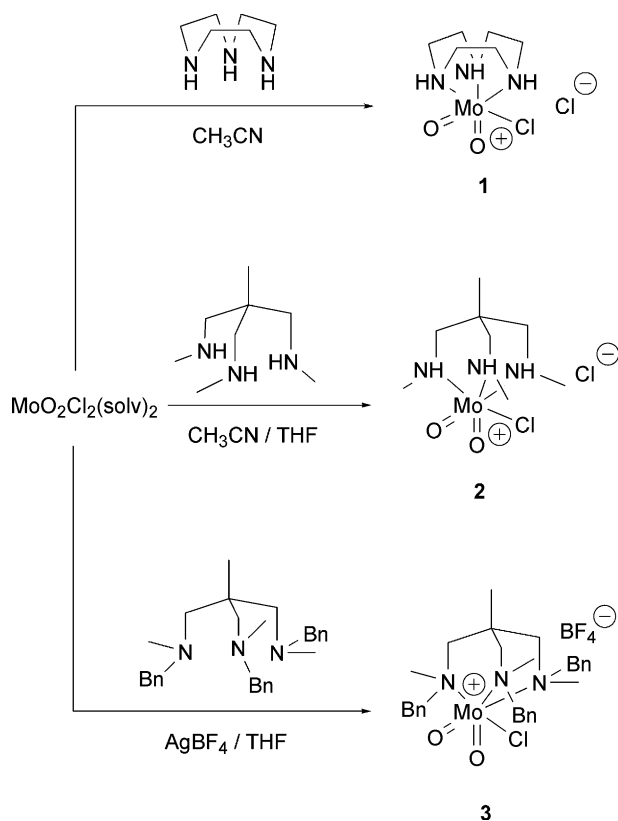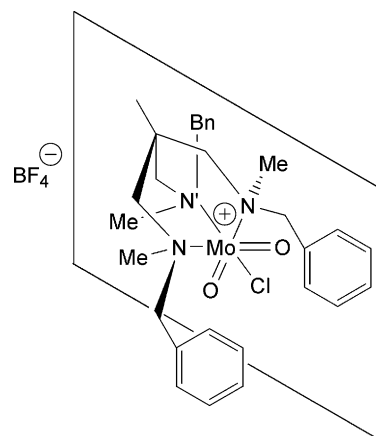

Scheme 1.

Fig. 1. Complex **3**, showing the symmetry plane indicated by the ^{1}H NMR spectrum.

the ligand to the metal centre. As a result, the capacity of the N-donor ligand to donate electron density to the electron deficient molybdenum atom may be reduced, and the Mo–O bond strengths will be higher.

Oxidative decarbonylation of tricarbonyl complexes of the type $LM(CO)_3$ (M = Mo, W) bearing tridentate N-ligands can lead to the corresponding trioxometal(VI) complexes LMO_3 [31–33]. For example, Roy and Wieghardt showed that the complexes $(tacn)M(CO)_3$ (M = Mo, W) react with H_2O_2 in tetrahydrofuran to yield essentially quantitatively $(tacn)MO_3$ [31]. We were interested to see whether complexes of the type $LM(CO)_3$ could be used directly as catalyst precursors in olefin epoxidation, in a manner similar to that already established for the $(\eta^5\text{-}C_5R_5)Mo(CO)_3Cl$ complexes. Reaction of Me_3-tame with the hexacarbonyls $Mo(CO)_6$ and $Cr(CO)_6$ in decaline at 130 °C gave the new complexes $(Me_3\text{-}tame)Mo(CO)_3$ (4) and $(Me_3\text{-}tame)Cr(CO)_3$ (5) as yellow powders in good yields (Eq. (1)). These tricarbonyl derivatives are indefinitely stable when stored under nitrogen, and in fact show no sign of decomposition when exposed to air and moisture, at least within 24 h. The infrared spectra of compounds 4 and 5 consist of several strong bands assigned to the C–O stretch (1892, 1776 and 1721 cm^{-1} for 4; 1890, 1766, 1738 and 1713 cm^{-1} for 5). In contrast, the analogous complex $(tacn)M(CO)_3$ exhibits only two $\nu(CO)$ bands consistent with the $\nu_{sym}(A_1)$ and $\nu_{asym}(E)$ modes in C_{3v} symmetry [34]. Both of the ligands tacn and Me_3-tame coordinate facially in an octahedron, with the three carbonyl groups in cis positions. The observation of more than two $\nu(CO)$ bands for 4 and 5 indicates that asymmetric complexes are formed because of the presence of the hydrogen and methyl substituents on the nitrogen atoms.

$$M(CO)_6 \xrightarrow{\text{decaline, 130 °C}} \quad M = Mo\ (4),\ Cr\ (5) \qquad (1)$$
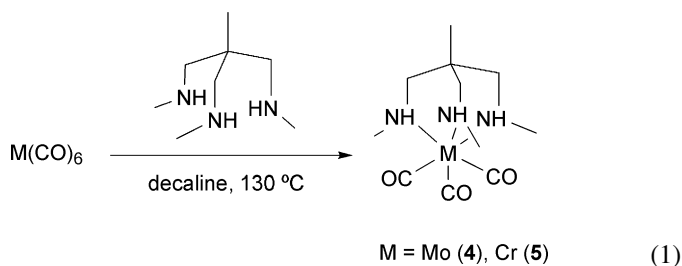
3.2. Catalytic tests

All of the compounds were tested as catalysts or catalyst precursors for the reaction of cis-cyclooctene with t-BuOOH (used as a 5.5 M solution in decane) at 55 °C, without additional solvent. The catalyst:substrate:oxidant molar ratio used was 1:100:150. Conversion of cyclooctene under the reaction conditions was only possible in the presence of a catalyst. Both cationic (1–3) and neutral (4,5) complexes formed colloidal solutions with the olefin and t-BuOOH. All of the catalytic runs yielded 1,2-epoxycyclooctane, which, with the exception of the molybdenum tricarbonyl complex 4, underwent consecutive epoxide ring-opening to give 1,2-cyclooctanediol.

The kinetic profiles for the ionic compounds 1–3 during the first 8 h of reaction are different from those of compounds 4 and 5 in that the conversion of cyclooctene is initially relatively fast,
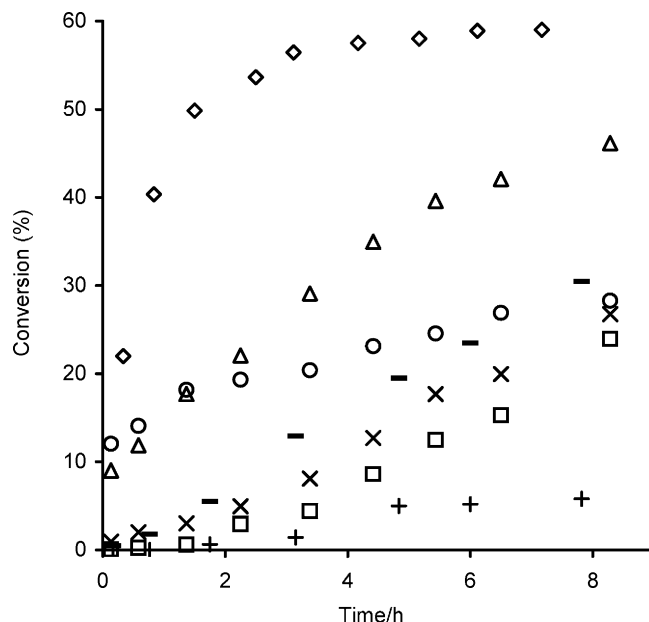

Fig. 2. Kinetic profiles of cyclooctene epoxidation with t-BuOOH in the presence of 1 (○), 2 (△), 3 (◇), 4 (□), 4′ (–), 5 (×) and 5′ (+).

but then slows down significantly as the reaction progresses (Fig. 2). $MoO_2X_2L_2$-type complexes also exhibit this kind of behaviour when used as epoxidation catalysts with t-BuOOH, suggesting that a similar reaction mechanism may be involved. The slowdown in the reaction rate for these complexes has been attributed to an auto-retardation effect where tert-butyl alcohol, a by-product of the epoxidation, is a competitive inhibitor of t-BuOOH for coordination to the Mo^{VI} centre [13]. The initial activities $(mol\ mol_{Mo}^{-1}\ h^{-1})$ follow the order 1 (90) > 2 (68) ≈ 3 (66) (calculated after 8 min reaction). However, for reaction times between 2 and 8 h, the trend is reversed and the catalytic activities increase in the order 1 < 2 < 3. Although it cannot be totally ruled out that the activities are due to significantly different species derived from the precursor complexes, it seems beyond reasonable doubt that the organic ligands remain, at least partially, attached to the metal in the catalytically active centre and determine its activity. The observed activities and selectivities for the epoxidation of cyclooctene are slightly inferior to those exhibited by the analogous complexes bearing tris(1-pyrazolyl)methane $[HC(pz)_3]$ and tris(3,5-dimethyl-1-pyrazolyl)-methane $[HC(3,5\text{-}Me_2pz)_3]$ ligands [9] (under similar reaction conditions, TOF = 270–300 $mol\ mol_{Mo}^{-1}\ h^{-1}$). The relative catalytic performances depend on the complex interplay of a number of factors, such as steric and electronic effects, solubility and hydrophilic–lipophilic balance. Steric hindrance might contribute to a lower activity, as it can make the co-ordination of the peroxide to the metal centre more difficult, and also hinders the approach of the olefin. The higher initial activity of complex 1 may therefore be partly due to lower steric constraints imposed on the reaction. We may further speculate that compounds 2 and 3 have similar initial activities because the enhanced steric effects caused by the extra benzyl groups in 3 are counterbalanced by a weaker metal–ligand interaction [as evidenced by the $\nu(Mo=O)$ stretching frequencies], which

would increase the Lewis acidity of the metal centre and increase catalytic activity. A higher Lewis acidity for complex **3** is also supported by the observation that the selectivity to the epoxide is lower than that for complex **2**, for conversions between 40 and 60% (Fig. 3). The initial catalytic activities for compounds **1**–**3** are comparable with those exhibited by MoO_2Cl_2L complexes containing 2,2'-bipyridine and 2,2'-bipyrimidine (25–$80 \, mol \, mol_{Mo}^{-1} \, h^{-1}$) [13], or ethylenediimine ligands such as N,N'-bis(benzylidene)ethylenediamine ($63 \, mol \, mol_{Mo}^{-1} \, h^{-1}$) [17]. MoO_2Cl_2L complexes containing diazabutadiene ligands such as N,N-p-tolyl-2,3-dimethyl-1,4-diazabutadiene generally exhibit higher activities ($180 \, mol \, mol_{Mo}^{-1} \, h^{-1}$) [14].

The kinetic profiles for the tricarbonyl precatalysts **4** and **5** show an initial induction period, and the initial specific activities are 1 and $7 \, mol \, mol_{Mo}^{-1} \, h^{-1}$, respectively (Fig. 2). This could be due to relatively slow oxidative decarbonylation of the complexes into high oxidation state oxo complexes, a step that occurs prior to the formation of the active oxidising agents. When oxidative decarbonylation of the molybdenum complex **4** with t-BuOOH was carried out prior to catalysis and the resulting compound (**4′**) was used for cyclooctene conversion, the initial reaction rate ($3 \, mol \, mol_{Mo}^{-1} \, h^{-1}$) was only slightly higher than that observed for **4**, while between reaction times of 1 and 8 h the conversions in the presence of **4′** were significantly higher than those achieved using **4** directly (Fig. 2). After 24 h the conversions were practically the same (65%) for both systems. Possibly, both the oxidative decarbonylation steps (for **4**) and the reaction of **4′** with t-BuOOH to give the active oxidising species are rather slow, accounting for the low initial reaction rate. An outstanding feature of compounds **4** and **4′** is that the selectivity to the epoxide is always 100% until ca. 80% conversion at 48 h (Fig. 3). In contrast, for the corresponding chromium complex **5**, the selectivity decreased drastically to about 50% and then

remained at this value for cyclooctene conversions between 10 and 70% (Fig. 3). The lower selectivity to the epoxide is probably due to the higher Lewis acidity of the active catalyst, which enhances the ring-opening reaction of the epoxide with water (present in the t-BuOOH solution, used as received, and in the air atmosphere of the reaction environment) to give the 1,2-diol. During the first 8 h the reaction rate is roughly the same for **4** and **5**, but thereafter conversion up to 48 h was higher for **4**. After a catalytic run with the Cr complex **5** a brown solid residue was obtained which may have resulted from the partial decomposition of the catalyst. When the oxidative decarbonylation of **5** was carried out prior to catalysis the resulting compound (**5′**) led to 10% conversion after 24 h compared to 33% for **5**, suggesting that this compound is unstable under the applied oxidative conditions (Fig. 2).

This study was further extended to the epoxidation of several different linear and cyclic olefins using complexes **2**–**4** (Table 1). For all of the compounds the catalytic activity tends to decrease as the olefin becomes less substituted and, therefore, less reactive: cyclododecene > ((R)-(+)-limonene, α-pinene) > trans-2-octene > 1-octene. In general, conversion at 24 h is higher for **2** and **3** than for **4**. On the other hand, epoxide yields at 24 h are higher for **4**. For example, at 28–37% conversion of cyclododecene, selectivity to the corresponding epoxide is 100% for **4**, 23% for **3** and 64% for **2**. Complexes **2** and **4** catalyse the mild and highly chemoselective (100% at ca. 17% conversion) epoxidation of (R)-(+)-limonene to limonene

Table 1
Cyclooctene epoxidation using t-BuOOH and the molybdenum complexes **2**–**4**[a]

Olefin	Complex	Conversion (%)	Selectivity to epoxide (%)
cis-Cyclooctene	**2**	75	82[b]
	3	61	74
	4	64	100
Cyclododecene	**2**	30	64[b]
	3	37	23
	4	28	100
1-Octene	**2**	8	0[c]
	3	7	0
	4	1	13
trans-2-Octene	**2**	10	50[d]
	3	8	0
	4	6	100
(R)-(+)-limonene	**2**	16	100[e]
	3	34	84[f]
	4	18	100[e]
α-Pinene	**2**	20	0[g]
	3	28	0
	4	12	54

[a] Reaction time = 24 h.
[b] The corresponding diol was formed.
[c] Heptanal was formed.
[d] Hexanal was formed.
[e] Selectivity to limonene oxide.
[f] Selectivity to limonene oxide plus 8,9-epoxy-p-menth-1-ene.
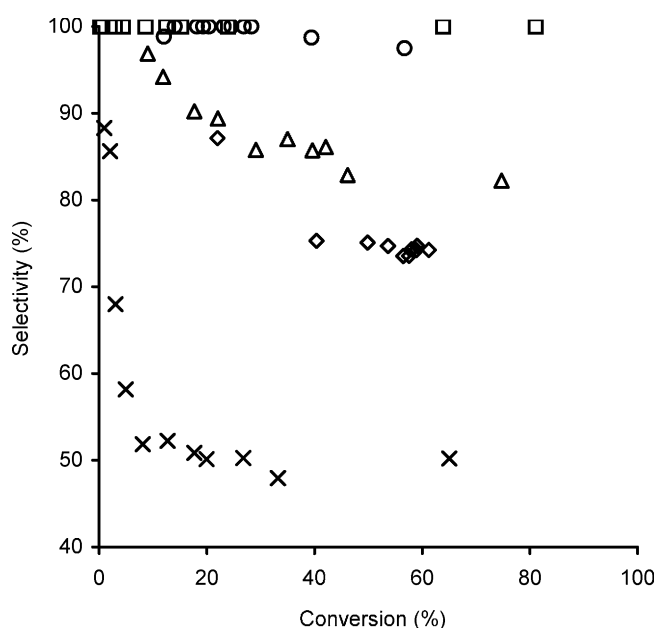[g] Selectivity to pinene oxide. Campholenic aldehyde, 1-verbenone and minor amounts of myrtenal were formed.

Fig. 3. 1,2-Epoxycyclooctane selectivity as a function of cyclooctene conversion in the presence of **1** (○), **2** (△), **3** (◇), **4** (□) and **5** (×).

oxide. For 1-octene and α-pinene using either complexes **2** or **3**, the reaction yields mainly heptanal and campholenic aldehyde, respectively, and no epoxides were obtained after 24 h.

4. Conclusions

The tridentate N-ligands tacn, Me$_3$-tame and Bn$_3$Me$_3$-tame form moderately active dioxomolybdenum(VI) catalysts for the epoxidation of olefins using t-BuOOH. In all of these complexes, the co-ordination strength of the ligand depends on its electron donor capability and steric bulk, and these properties clearly affect the catalytic performance. Different substituents on the nitrogen atoms of the tacn and tame ligands may therefore further improve the catalytic activity of these systems. We have also shown that the tricarbonyl compounds (Me$_3$-tame)M(CO)$_3$ (M = Mo, Cr), which are easily available from M(CO)$_6$, are precursors to catalysts for the oxidation of olefins to epoxides. Like the related (η^5-C$_5$R$_5$)Mo(CO)$_3$Cl complexes, the parent tricarbonyl compounds can be used directly since under the applied reaction conditions they undergo oxidative decarbonylation into high oxidation state oxo complexes. The catalytic activities were modest, due in part to the existence of induction periods, but selectivities to the epoxides were generally high in the presence of the Mo compound.

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