Catalysis Science & Technology

PAPER



Cite this: DOI: 10.1039/c5cy02052b

Oxidomolybdenum complexes for acid catalysis using alcohols as solvents and reactants[†]

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The application field of dichloridodioxidomolybdenum(vi) chelate complexes, which have been intensively investigated as catalysts for liquid-phase olefin epoxidation, is broadened to encompass acid catalysis, in particular, alcoholysis and acetalisation reactions. Complex $[MoO_2Cl_2(L)]$ (1) with L = 4,4'-di-*tert*-butyl-2,2'-bipyridine was chosen as (pre)catalyst. Depending on the reaction conditions, 1 either remained structurally intact or was transformed into different metal species, the structures of which were determined on the basis of single-crystal X-ray diffraction, spectroscopic techniques (FT-IR and ¹H NMR), and elemental analysis. The first example of a mixed-ligand complex of the type $[MoO_2X(OR)(L)]$ (X = halide) is disclosed. This complex is one of only a handful of complexes known to date that exhibit an all-*cis* configuration instead of the usual *cis*-oxido, *trans*-X, *cis*-L configuration (X = anionic ligand). Mechanistic considerations of the formation of the metal species are made.

Received 27th November 2015, Accepted 18th March 2016

DOI: 10.1039/c5cy02052b

www.rsc.org/catalysis

Introduction

The oxychloride MoO₂Cl₂ has been intensively studied over the years as a catalyst for a wide variety of organic transformations involving, for example, oxidations, activation of X-H (X = Si, B, P and H) bonds, C-X bond forming reactions, and in the reduction of a variety of functional groups.¹ In many cases the catalyst used is a solvent adduct of the type $[MoO_2Cl_2(S)_2]$ (S = DMF, THF, DMSO). The solvent molecules in these adducts are readily replaced by Lewis base ligands (L) to give complexes of the type $[MoO_2Cl_2(L)_n]$. A wide variety of complexes containing bidentate nitrogen-donor ligands have been prepared and studied, such as those with 2,2'-bipyridine (bipy) and its derivatives,² 1,4-diazabutadienes,^{2a,3} ethylenediimines,⁴ oxazolines,⁵ pyridylimines,⁶ pyrazolylpyridines,⁷ and pyrazolylpyrimidines.⁸ Catalytic studies with these complexes have essentially been limited to liquid-phase olefin epoxidation using alkylhydroperoxides as oxidants. Very active and selective catalysts have been

obtained through optimisation of the type of organic ligand and the associated substituents. $^{2\!f}$

In the present work, we set out to widen the field of organic transformations catalysed by dichloridodioxidomolybdenum(vi) complexes. The complex [MoO₂Cl₂(di-tBu-bipy)] (1) (di-tBu-bipy = 4,4'-di-tert-butyl-2,2'-bipyridine) was chosen as the (pre)catalyst. Several published studies demonstrate that di-tBu-bipy is a good choice as a ligand for oxometal complexes to be used as catalysts for organic transformations.⁹ For example, in addition to the mononuclear complex 1, which was first reported as an olefin epoxidation catalyst in 2000,^{2a} the $[MoO(O_2)_2(di-tBu-bipy)]$,^{9a} $[MoO_2(NCS)_2(di-tBu$ complexes bipy)],^{9b-9e} $[Mo_2O_4(\mu_2-O)X_2(di-tBu-bipy)_2]$ (X = Cl, NCS),^{9a,e} $[Mo_2O_6(di-tBu-bipy)_2]$,^{9f} and $[V_2O_2(\mu-MO_2)_2(\mu-MO_4)_2(di-tBu-bipy)_2]$ $bipy_{2}$ (M = Mo, W)^{9k} are effective as oxygen atom transfer agents and/or (pre)catalysts for alcohol oxidation and olefin epoxidation. Kodama et al. concluded that the affinity of the heterotetranuclear V2W2 complex to organic substrates was improved by the selection of di-*t*Bu-bipy as the organic ligand.^{9k}

Complexes of the type $[MoO_2Cl_2(L)_n]$ possess Lewis acid character, which plays a key role in defining the reaction mechanism for olefin epoxidation with alkylhydroperoxides.^{1*a,b*} We therefore chose to study two reactions typically catalysed by Brønsted or Lewis acids, namely the acetalisation of benzaldehyde with ethanol, and the ringopening reaction of styrene oxide with ethanol. Acetalisation is often used in organic synthesis to protect the carbonyl group of aldehydes and ketones, since 1,3-dioxolanes are stable under neutral and basic conditions.¹⁰ Besides the interest in acetals as protecting groups, they are interesting for their

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[†] Electronic supplementary information (ESI) available: Powder XRD patterns, FT-IR and GC-MS data, crystal packing descriptions, tabulated crystallographic data and additional figures. CCDC 1435952 (2), 1435953 (4-5CHCl₃) and 1435954 (4-2EtOH). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cy02052b

use in pharmaceuticals and as fragrances in soaps and perfumes.^{10,11} Regarding the second reaction studied, epoxide ring-opening is a frequently used transformation in organic synthesis.¹² In particular, ring-opening reactions of epoxides with alcohols provide a synthetically important path to β -alkoxyalcohols, which are important moieties in many biologically active molecules, and can be employed as valuable organic solvents, natural products, or intermediates, in organic and inorganic synthesis.¹³

Although Lewis base adducts of the type [MoO₂Cl₂(L)] bearing bidentate nitrogen-donor ligands are generally considered to be quite stable, the Mo-Cl bond is susceptible to cleavage, especially in the presence of water.^{7c,d,9h} In a recent study, the oxido-bridged dinuclear complex $[Mo_2O_4(\mu_2 - \mu_2)]$ O) $Cl_2(pypzEA)_2$] (pypzEA = ethyl[3-(pyridin-2-yl)-1H-pyrazol-1yl]acetate) was obtained in significant yield upon treatment of [MoO₂Cl₂(pypzEA)] with ethanol.¹⁴ Hence, in the present work, a particular emphasis was placed on examining the stability of 1 in alcohol solvents in order to identify the main species responsible for the catalytic reactions. We show that, depending on the reaction conditions, 1 is transformed into other species, including an unprecedented molybdenum(vi) oxidoalkoxido complex, dinuclear oxido-bridged complexes, and an octanuclear complex. The crystal structures of some of these species have been determined.

Results and discussion

Stability experiments in ethanol

In parallel with the catalytic studies (described below), contact tests (CTs) were performed to investigate the stability of the mononuclear Mo^{VI} complex $[MoO_2Cl_2(di-tBu-bipy)]$ (1) in the presence of alcohols (ethanol, tert-butanol, and 1-phenylethanol) at different temperatures (without organic substrate). Studies on the stability of 1 in the presence of ethanol solutions containing organic substrates (benzaldehyde, styrene oxide, 1-phenylethanol and 2-phenylethanol) are described below in the catalysis sections. The CT performed under conditions equivalent to those used in the catalytic tests (20 µmol 1, 1 mL EtOH, 55 °C, 24 h) gave a suspension. The solid (1/CT-sol) was isolated by filtration, washed with pentane, and dried. Addition of pentane to the filtrate, followed by storage of the mixture at 4 °C overnight, led to a colourless precipitate (1/CT-liq), which was filtered, washed with pentane, and dried. The ATR FT-IR spectra of 1/CT-sol and 1/CT-liq matched that for 1 (Fig. 1) suggesting that the complex is quite stable under these conditions. Similar results were obtained when the contact test was performed on a larger scale (0.32 mmol 1, 20 mL EtOH).

In contrast to the results at 55 °C, complex 1 underwent fairly rapid transformations when treated with ethanol under reflux (large-scale contact test, LSCT). A bordeaux-coloured precipitate formed during 24 h, which was isolated and identified as the Mo^V oxido-bridged dinuclear complex [Mo₂O₂(μ_2 -O)Cl₄(di-*t*Bu-bipy)₂] (3) (Scheme 1) on the basis of FT-IR, ¹H NMR and elemental analysis data (discussed in more detail



Fig. 1 ATR FT-IR spectra in the range $350-1750 \text{ cm}^{-1}$ of (a) complex 1, (b) 1/CT-liq, (c) 1/CT-sol, (d) 1/BzA-liq, (e) 1/BzA-sol, (f) 1/PhEtOH-liq, (g) 1/PhEtOH-sol, (h) 1/StyOx-liq, (i) complex 6, (j) 6/StyOx-liq, (k) 5/StyOx-liq, (l) 2/StyOx-liq, (m) 4/StyOx-liq, and (n) complex 4.

below). Vapour diffusion of pentane into the mother liquor obtained in this reaction gave a small number of yellow and orange crystals, which were mechanically separated and subjected to X-ray diffraction analyses (see below). The yellow crystals were identified as the MO^{VI} oxidoalkoxido complex [MoO₂Cl(OEt)(di-*t*Bu-bipy)] (2), while the orange crystals were found to comprise the MO^{V} oxido-bridged dinuclear complex [Mo₂O₂(μ_2 -O)₂Cl₂(di-*t*Bu-bipy)₂]-2EtOH (4·2EtOH). In addition, a small amount of a bordeaux-coloured solid precipitated, which was identified as a mixture comprising complexes 1 (*ca.* 10 mol%), 2 (*ca.* 80 mol%) and 3 (*ca.* 10 mol%) by ¹H



NMR (combined yield of 15% based on Mo). A comparison of the powder X-ray diffraction (PXRD) pattern of the bordeaux precipitate with a simulated pattern calculated from the single-crystal X-ray structural data for 2 confirmed that the major component was complex 2 (ESI,† Fig. S1).

 Mo^{VI} oxidoalkoxido complexes of the type $[MoO_2(OR)_2(L)]$ are quite scarce, even though complexes with R = iPr and *t*Bu, and L = bipy, were reported in 1984 by Chisholm *et al.*,^{15*a*} followed later by reports describing the complexes with OR = allyloxo and L = bipy,^{15*b*} and OR = diacetoneglucose and L = 1,10-phenanthroline (1,10-phen).^{15*c*} To the best of our knowledge, complex 2 is the first example of a mixed-ligand complex of the type $[MoO_2X(OR)(L)]$ (X = halide). Furthermore, as will be described below in the section devoted to the discussion of the crystal structures, the complex exhibits the extremely rare all-*cis* configuration instead of the far more common *cis*-oxido, *trans*-X, *cis*-L configuration.

Mechanistic considerations of the transformation of 1

Complex 3 was previously isolated from the reduction of 1 with H_2 in toluene.^{16a} Key IR bands for 3 at 964 cm⁻¹

[v(Mo=O)] and 786 cm⁻¹ [v(Mo-O-Mo)] (ESI,† Fig. S2) are in agreement with those reported by Reis and Royo,^{16a} and with values reported for analogous complexes containing other bidentate heterocyclic amines, e.g. 966 and 801 cm⁻¹ for $[Mo_2O_2(\mu_2-O)Cl_4(bpym)_2]$ (bpym = 2,2'-bipyrimidine),^{16b} and 966 and 798 cm⁻¹ for $[Mo_2O_2(\mu_2-O)Cl_4(bipy)_2]$.^{16c} The formation of 3 from 1 in significant amount (63% yield for the reaction performed under reflux) is somewhat surprising but can be attributed to the propensity of ethanol to function as both a solvent and a reducing agent. Indeed, reduced metallo-organic complexes are often prepared by reacting a complex with the metal in a higher oxidation state with ethanol^{17*a*} (e.g., $Pt^{IV} \rightarrow Pt^{II}$, $h^{III} \rightarrow Rh^{I}$, $h^{III} \rightarrow Rh^{II}$, $h^{III} \rightarrow Rh^{III}$, $h^{IIII} \rightarrow Rh^{III}$, $h^{III} \rightarrow Rh^{III}$, $h^{III} \rightarrow Rh^{III}$, h^{III Ru^{II}, ^{17d}). Also, alcohols are widely used in nanoparticle preparations.¹⁸ As noted previously,^{16a} the formation of 3 is likely the result of the reduction of 1 to the oxidomolybdenum(IV) species [MoOCl₂(di-tBu-bipy)], followed by comproportionation. This is consistent with the well known tendency of oxidomolybdenum(IV) and dioxidomolybdenum(VI) species to associate leading to stable comproportionation products of oxidomolybdenum(v), which are more resistant to reduction.¹⁹ We may further propose that the Mo^{VI} oxidoalkoxido complex 2 could be an intermediate in the formation of [MoOCl₂(di-tBu-bipy)] (Scheme 2). H-abstraction from the coordinated ethoxide could lead to liberation of acetaldehyde and formation of [MoO(OH)Cl(di-tBu-bipy)], which in the presence of HCl may give [MoOCl2(di-tBu-bipy)] and water. Such a mechanism parallels that generally presented for the oxidation of ethanol to acetaldehyde over supported molybdenum oxide catalysts.²⁰ The water formed in this reaction will likely contribute to the eventual hydrolysis of 3 to give 4. Indeed, as noted above, single crystals of the ethanol solvate 4.2EtOH were isolated from the mother liquor of the reaction of 1 in refluxing ethanol.

Some further support for the mechanistic considerations discussed above was obtained by treating complex 1 in refluxing *tert*-butanol. Under these conditions, no bordeaux-coloured solid formed during 24 h (the undissolved solid phase was identified as 1 by FT-IR spectroscopy), and the pink-coloured solid obtained after addition of pentane to the reaction solution was identified as the Mo^{VI} oxido-bridged di-



Scheme 2 Possible pathways for the sequential formation of complexes 2–4 from 1 (L = di-tBu-bipy) in ethanol.

nuclear complex $[Mo_2O_4(\mu_2-O)Cl_2(di-tBu-bipy)_2]$ (5) (obtained in a low yield of 7%) by FT-IR spectroscopy and PXRD. The PXRD pattern of the bulk product 5 was in good agreement with a simulated pattern calculated from the single-crystal X-ray structural data published for the hydrate 5.0.2H₂O (ESI,† Fig. S1).²¹ The formation of 5 in a low yield can be attributed to the presence of a residual amount of water in the solvent. Taking into account the above discussion concerning the reducing behaviour of ethanol, the failure to observe the formation of either of the Mo^V dinuclear complexes 3 or 4 upon treatment of 1 with tert-butanol is not surprising since the latter has no α -hydrogen available for abstraction, preventing any subsequent reduction step. Accordingly, in contrast to ethanol, tert-butanol was found to be ineffective for the preparation of colloidal rhodium through the reduction of rhodium(III) chloride.^{18a} Additional reactions were performed in which complex 5 was treated with ethanol at either 55 °C or under reflux overnight. At the lower temperature, 5 was recovered unchanged, while at the higher temperature an orange solid (identified as 4) was isolated. We may propose that at the higher temperature 5 reacts with one molecule of ethanol to give 2 and an intermediate of the type [MoO₂(OH)Cl(di-tBu-bipy)]. In a manner equivalent to that proposed above for the formation of 3, 2 could give acetaldehyde and [MoO(OH)Cl(di-tBu-bipy)], which may react with $[MoO_2(OH)Cl(di-tBu-bipy)]$ to give the Mo^V complex 4 and one molecule of water.

To study the stability of 1 in alcohol media at higher temperatures, 1-phenylethanol was used at 55 and 130 °C (for 24 h). At the lower temperature, a bordeaux precipitate (3) and an orange solution (containing 4) were obtained, similar to the behaviour with ethanol under reflux. At 130 °C, an orange-red solution was obtained with no undissolved solid. Addition of pentane led to the precipitation of the Mo^V dinuclear complex 4 as an orange solid in 73% yield. The remaining 1-phenylethanol/pentane solution was analysed by GC-MS, which revealed the presence of acetophenone (ESI,† Fig. S3). Hence, like ethanol, 1-phenylethanol can function as both a solvent and a reducing agent, being oxidised in this case to acetophenone. This has been noted in other works such as the preparation of palladium organosols by reduction of palladium acetate in the presence of polyvinylpyrrolidone.²² Key IR bands for 4 at 956 cm⁻¹ [ν (Mo=O)], 935 cm⁻¹ [v(Mo=O)] and 728 cm⁻¹ [v(Mo-O-Mo)] (ESI,[†] Fig. S2) are in agreement with those reported for analogous complexes containing other bidentate heterocyclic amines, e.g. 955, 934 and 735 cm⁻¹ for [Mo₂O₂(µ₂-O)₂Cl₂(bpym)₂],^{16b} and 954, 935 and 738 cm⁻¹ for [Mo₂O₂(µ₂-O)₂Cl₂(1,10-phen)₂].²³ Recrystallisation of 4 from chloroform/hexane gave orange crystals of the chloroform solvate 4.5CHCl₃ suitable for structure determination by X-ray diffraction (see below).

Crystal structures of complexes 2 and 4

Compounds 2 and 4 were isolated as single-crystals appropriate for XRD analysis, being unequivocally formulated as [MoO₂Cl(OEt)(di-*t*Bu-bipy)] (2), [Mo₂O₂(μ_2 -O)₂Cl₂(di-*t*Bu-bipy)₂] ·2EtOH (4·2EtOH) and [Mo₂O₂(μ_2 -O)₂Cl₂(di-*t*Bu-bipy)₂]·5CHCl₃ (4·5CHCl₃) (see Experimental section for details). Complex 2 crystallised in the monoclinic space group $P2_1/c$ with the asymmetric unit (asu) only including the mononuclear complex [MoO₂Cl(OEt)(di-*t*Bu-bipy)], while complex 4 crystallised in two distinct crystal systems depending on the nature of the solvent used: 4·2EtOH crystallised in the triclinic space group $P\overline{1}$ with one dinuclear complex [Mo₂O₂(μ_2 -O)₂Cl₂(di*t*Bu-bipy)₂] and two EtOH molecules of crystallisation comprising the asu; 4·5CHCl₃ crystallised in the cubic space group $Fd\overline{3}c$ in which the asu is composed of half of the complex unit and 2.5 molecules of CHCl₃ (ESI,† Fig. S4).

The molecular structure of the Mo^{VI} oxidoalkoxido complex 2 is depicted in Fig. 2. The unique Mo^{VI} centre has distorted octahedral geometry due to coordination of two N-atoms of one di-*t*Bu-bipy molecule, two terminal oxido groups, one ethoxido ligand and one chlorido ligand, {MoClN₂O₃}. As usual, the two Mo=O bonds [1.633(3) and 1.699(5) Å] are considerably shorter than the remaining Mo-O, Mo-N and Mo-Cl, and markedly exert their *trans*-effect on the opposite single bonds (ESI,† Table S2). This is evident in the two different bond lengths found for Mo-N1 [2.253(4) Å] and Mo-N2 [2.316(3) Å]. The high distortion of the octahedral coordination environment of the Mo^{VI} centre is clearly apparent from an analysis of the internal bond angles: the *cis* an-



grise 2 Molecular structures of the (a) mononuclear complex [MoO₂Cl(OEt)(di-tBu-bipy)] (2) and (b) dinuclear complex [Mo₂O₂(µ₂-O)₂Cl₂(di-tBu-bipy)₂] (4; present in compound 4·2EtOH), showing the labelling scheme for all atoms composing the Mo coordination environments. H-atoms have been omitted for clarity. Detailed information about the bond lengths and angles of the Mo coordination centres is summarised in Tables S2 and S3 in the ESI.†

gles are found in the 69.79(11)–106.8(2)° interval, while the *trans* angles range between 154.9(2) and 161.09(9)° (Table S2†). The Mo1 atom is displaced by *ca.* 0.24 and 0.50 Å from the equatorial plane and geometrical centre of the coordination, respectively.

The molecular structure of complex 2 is highly unusual since the ligands adopt an all-cis configuration, that is, cis-oxido, cis-X, cis-L (X = Cl, OEt). Complexes of the type $[MO_2X_2(L)_n]$, where L is either a neutral bidentate (n = 1) or monodentate (n = 2) ligand, display almost exclusively a *cis*, trans, cis arrangement in which the weaker donor atoms belonging to L are found to be *trans* to the terminal oxygen atoms, where they are not directly competing for the available empty metal d orbitals.²⁴ Only a handful of complexes with the all-cis configuration have been reported, namely $[MO_2Cl_2(tmen)]$ (M = Mo, W; tmen = N,N,N',N'tetramethylethylenediamine), 25a,b [MoO₂Cl₂(tmc)] (tmc = tetramethylcyclam),^{25c} dinuclear [Mo₂O₄Cl₄{o-C₆H₄(CH₂SMe)₂]₂],^{25d} the oxido-bridged dinuclear complex $[Mo_2O_4(\mu_2-O)Cl_2(pyrazole)_4]$,^{25e} $[MoO_2(L)]$ (L = 1,4-diazepane-based bis(phenolate) ligand),^{25f} and $[MoO_2(L)_2]$ (L = aryloxide-pyrazole ligand).^{25g} A computational investigation of the relative stabilities of the two different isomers of [MoO₂Cl₂(tmen)] led to the conclusion that steric effects (involving repulsive interactions between the chelating ligand and the two ligands perpendicular to the N-Mo-N plane) could override the electronic preference for the cis, trans, cis isomer.^{24a} For complex 2, steric destabilisation of the cis, trans, cis isomer may arise from unfavourable interactions between the ethoxido group and tert-butyl groups in the same molecule and/or in neighbouring molecules.

The crystal structure of complex 4, $[Mo_2O_2(\mu_2-O)_2Cl_2(di$ tBu-bipy)2], reveals a Mo^V oxido-bridged dinuclear complex (Fig. 2b and ESI,† Fig. S4). The Mo^V centres are interconnected by two µ2-bridging oxido groups, imposing Mo…Mo distances of 2.5625(2) and 2.5686(2) Å for the compounds 4.2EtOH and 4.5CHCl₃, respectively. These distances are indicative of Mo-Mo single bonds resulting from a d¹-d¹ (Mo^V-Mo^V) interaction.^{26a,b} The Mo-O-Mo angles involving the μ_2 -bridging oxido groups are 83.050(5) and 83.205(5)° for 4.2EtOH, and 83.06(1)° for 4.5CHCl3, which are in good agreement with those previously reported for similar complexes.^{19b,26b-d} For the complex in 4·2EtOH, the two crystallographically independent Mo^V centres have identical distorted octahedral coordination environments, being connected to two N-atoms of one di-tBu-bipy ligand, two µ2bridging oxido groups, one terminal oxido group and one chlorido ligand, {MoClN₂O₃}. The significant degree of distortion verified in the coordination geometries of Mo1 and Mo2 is confirmed by the bond lengths and internal octahedral angles (ESI,† Table S3): as expected, the Mo=O distances [Mo1-O1 = 1.687(3) Å, Mo2–O4 = 1.687(3) Å] are shorter than the Mo–O distances for the μ_2 -O bridges, which range from 1.913(3) to 1.947(3) Å; the distances of the Mo-N bonds in the position trans relative to the terminal Mo=O bonds [2.319(3) and 2.303(3) Å] are considerably longer than those

which are *trans* to the μ_2 -O bridges [2.235(3) and 2.229(3) Å], as a consequence of the trans effect of Mo=O; the cis and trans internal octahedral (Cl,N,O)-Mo-(Cl,N,O) angles range from 70.61(12) to 112.04(13)°, and from 156.45(13) to 160.30(9)°, respectively, revealing considerable dispersion around the expected values for regular octahedral environments. In the complex of 4.5CHCl₃, the unique crystallographically independent Mo centre (Mo1) has a similar environment to that described for Mo1 and Mo2 in 4.2EtOH, also coordinating to two N-atoms of one di-tBu-bipy ligand, two μ_2 -bridging oxido groups, one terminal oxido group, and one chlorido ligand, {MoClN₂O₃} (ESI,† Fig. S4). In fact, the Mo1 coordination centre exhibits a highly distorted overall octahedral geometry with the Mo1-Cl,N,O bond lengths and (Cl,N, O)-Mo-(Cl,N,O) angles being comparable to those of 4.2EtOH (ESI,† Table S4).

A full account of the crystal packing for 2, 4·2EtOH and 4·5CHCl₃, including figures and details of hydrogen bonding geometries, is provided in the ESI.[†]

Acid-catalysed acetalisation of benzaldehyde using 1

Complex 1 was tested for the acetalisation of benzaldehyde with ethanol at 55 °C (Scheme 3). To the best of our knowledge, the use of Mo-based complexes in this reaction has not been previously reported, and there are no studies involving different transition metal complexes bearing bipyridine-type ligands. The catalytic reaction was very fast, reaching ca. 86% conversion at 10 min, and benzaldehyde diethyl acetal was formed with 100% selectivity. Without catalyst the reaction was sluggish (4% conversion at 10 min). These results point to the role of 1 as a Lewis acid catalyst in the acetalisation mechanism. According to studies reported in the literature for Lewis acid-catalysed acetalisation reactions, the overall mechanism may involve the intermediate formation of a hemiacetal.^{11d,27} No intermediates were detected for the catalytic system 1/benzaldehyde/ethanol, which may be due to their relatively high reactivity under the catalytic reaction conditions used.

Benzaldehyde conversion reached a plateau at *ca.* 10 min, which can be attributed to thermodynamic limitations associated with the reversible acetalisation process, *i.e.* water is formed as a co-product and the acetal can be hydrolysed back to the aldehyde.^{11a,d,27a} In an attempt to shift the equilibrium

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to the right by continuously removing water from the reaction medium, activated 3 Å molecular sieves were added to the reaction mixture together with 1. The reaction stopped at 10 min and conversion was only slightly higher (89%) than that reached in the absence of molecular sieves (86%). More efficient removal of water from the reaction medium may lead to further improvements in conversion.

The system of 1/benzaldehyde/ethanol consisted of a biphasic mixture, specifically a colourless transparent liquid phase and a solid phase. The solids recovered after 24 h (as described in the Experimental section) were characterised by ATR FT-IR spectroscopy and PXRD; 1/BzA-sol and 1/BzA-liq denote the metal species which were undissolved and dissolved in the reaction medium, respectively. As found for the contact tests (CTs) performed in the absence of substrate (1/CT-sol and 1/CT-liq, discussed above), the recovered solids and original complex 1 exhibited similar FT-IR spectra (Fig. 1) and PXRD patterns (ESI,† Fig. S10), suggesting that complex 1 was essentially the active species responsible for the acetalisation reaction.

Acid-catalysed alcoholysis of styrene oxide using 1

Complex 1 was further explored for the acid-catalysed ringopening reaction of styrene oxide (StyOx) with ethanol at 55 °C (Scheme 4). The corresponding β-alkoxyalcohol product, namely 2-ethoxy-2-phenylethanol (EPE), was formed with 100% selectivity at 98% conversion, 24 h reaction (Fig. 3). Without catalyst, the conversion was only 5% at 24 h. Hence, the alcoholysis reaction was promoted by Lewis acid molybdenum species. To the best of our knowledge, there are only two studies reported in the literature on the use of molybdenum-based homogeneous catalysts for this reaction,²⁸ and there are no studies involving different transition metal complexes bearing bipyridine-type ligands. Specifically, the ethanolysis of StyOx was carried out in the presence of [MoO₂Cl₂], which led to 92% EPE yield after 2 h reaction at room temperature (conversion and selectivity were not indicated, and catalyst stability was not addressed).^{28a} In the other study, cyclopentadienyl molybdenum carbonyl complexes were tested as pre-catalysts for ethanolysis of StyOx at 55 °C (using higher catalyst concentration), which led to 100% EPE selectivity, and in terms of reaction rate, the best result was reported for $[(\eta^5-C_5H_4COOH)Mo(CO)_2(\eta^3 C_3H_5$] which gave a turnover frequency of 61 mol mol_{Mo}





Scheme 4 Acid-catalysed ethanolysis of styrene oxide.



Fig. 3 Acid-catalysed alcoholysis of styrene oxide with ethanol at 55 °C in the presence of compounds 1 (\Diamond), 2 (×), 4 (\triangle), 5 (\Box) and 6 (+).

 $h^{-1},$ which is similar to that for compound 1 (56 mol $mol_{Mo}{}^{-1} h^{-1}).{}^{28b}$

For comparison, compounds 2, 4 and 5 were also examined for the reaction of StyOx under similar conditions to those used for 1 (Fig. 3). For the tested compounds, EPE was always the only reaction product, and initial reaction rate was highest for 1. The differences in catalytic results may be due to various factors, including differences in intrinsic activities, initial dissolution rates and solubility of the starting compound, catalyst stability (discussed ahead) and kinetics of formation/conversion of metal species, which can influence the overall kinetics of the catalytic reaction in complex fashions. Nevertheless, all kinetic curves tended to similar conversion at 24 h reaction (94–98%).

For the catalytic system using 1, no condensation products (ethers) of the alcohol solvent were detected. The same was observed when 1-phenylethanol or 2-phenylethanol were used (instead of StyOx) as model hydroxylated substrates, i.e., no reaction took place during 24 h at 55 °C. These results, together with the excellent regioselectivity toward the β-alkoxyalcohol product formed from the epoxide substrate StyOx, suggest that the catalytic system can exhibit a carbon atom efficiency of 100% (since all the carbon atoms present in the reactants are incorporated into the product). A nucleophilic substitution mechanism may be involved in the conversion of StyOx to the corresponding β-alkoxyalcohol. According to the literature, the interaction between the oxygen atom of StyOx and the Lewis acid metal center (acid-base interaction) can lead to enhanced electrophilicity of the carbon atoms of the oxirane ring, facilitating the nucleophilic attack of an incoming alcohol molecule at the more substituted carbon atom to give a β-alkoxyalcohol product.13b,d,29

With the phenylethanol model substrate, the reaction mixtures were biphasic solid-liquid. As found for the biphasic catalytic system benzaldehyde/ethanol/1, ATR FT-IR (Fig. 1) and PXRD (ESI,† Fig. S10) data for the solids recovered from the liquid and solid phases of the reaction of 1-phenylethanol (denoted as 1/PhEtOH-liq and 1/PhEtOH-sol, respectively) were similar to those for 1.

In contrast to the biphasic systems 1/benzaldehyde/ethanol and 1/phenylethanol/ethanol, the system StyOx/ethanol/1 consisted of a transparent homogeneous pale vellow solution. The solution species in the StyOx reaction system were isolated by precipitation with pentane (as detailed in the Experimental section), and the resultant solid (1/StyOx-liq) was characterised by ATR FT-IR spectroscopy and PXRD. The solid 1/StyOx-liq was X-ray amorphous (PXRD not shown), whereas 1 was crystalline, and the FT-IR spectra of 1/StyOxliq and 1 were very different (Fig. 1). Hence, 1 was converted to different metal species during the StyOx catalytic process. Interestingly, the ATR FT-IR spectra of the solids (n/StyOx-liq with n = 2, 4 or 5) isolated from the liquid phase of the catalytic systems (2, 4 or 5)/StyOx/ethanol were practically identical to that for 1/StyOx-liq (Fig. 1). These results suggest that the same molybdenum-containing species was formed from the different complexes, which may partly explain the fact that the kinetic curves tended to similar conversion at 24 h reaction.

After comparing the FT-IR spectra of n/StyOx-liq (n = 1, 2, 2) 4 and 5) with spectra reported for other oxomolybdenum complexes containing the ligand di-tBu-bipy, including those obtained in the present work, it became clear that the spectra match very well with that exhibited by the octanuclear complex [Mo₈O₂₄(di-tBu-bipy)₄] (6) (Fig. 1). Previously, complex 6 had only been isolated after oxidative decarbonylation of molybdenum carbonyl complexes with tert-butylhydroperoxide, namely the complexes [Mo(CO)₄(di- $[Mo(CO)_{3}I_{2}(di-tBu-bipy)],^{30}$ *t*Bu-bipy)],^{9g} and $Mo(n^3-C_3-$ H₅)Cl(CO)₂(di-tBu-bipy)].^{9a} The molecular structure of 6 consists of a central cubane-type $Mo_4(\mu_3-O)_4$ core (Scheme 1).^{9a,g} Four peripheral $[MoO_2(di-tBu-bipy)]^{2+}$ units cap the long edges of the Mo4 tetrahedron of the central cubane to form the final windmill-type octanuclear complex. The formation of 6 in the StyOx/ethanol system at 55 °C is in stark contrast to the apparent stability of 1 in the benzaldehyde/ethanol and phenylethanol/ethanol systems at the same temperature, and is evidently associated with the rapid solubilisation of species in the StyOx/ethanol system to give a homogeneous solution. The presence of StyOx in excess at the beginning of the reaction (StyOx: Mo molar ratio of 20) is likely to be an important factor, possibly affecting the polarity of the medium. The conversion of 1 to 6 may involve dissociation of the chlorido ligands, and condensation reactions of monoand dinuclear intermediates possibly related to complexes 2-5. When complex 6 was examined for the reaction of StyOx under similar conditions to those used for 1, 2, 4 and 5, EPE was again obtained with 100% selectivity (Fig. 3). The initial reaction rate was much lower for 6 than for 1, but conversion at 6 h was highest for 6 (96% for 6 vs. 62% for 4 and 71-75% for 1, 2 and 5). For the reaction using 6, the ATR FT-IR

spectrum of the solid isolated from the liquid phase (denoted 6/StyOx-liq) was practically identical to that for 6 (Fig. 1).

The reaction of StyOx in the presence of physically mixed MoO_3 and di-*t*Bu-bipy (each in equivalent molar amounts to that used for 1) led to very poor catalytic results: 18% conversion at 24 h, and 92% EPE selectivity. The isolated metal species exhibited a similar ATR FT-IR spectrum to that of MoO_3 , suggesting that *in situ* complexation reactions between MoO_3 and di-*t*Bu-bipy did not occur. On the other hand, while complex 1 was *in situ* converted to 6, this was not the case for the physical mixture MoO_3/di -*t*Bu-bipy. It has been previously reported that harsh hydrothermal conditions are required to convert MoO_3 and di-*t*Bu-bipy into 6 (160 °C, 3 days, with agitation; 70% synthesis yield).^{9h}

Conclusions

In this work a number of valuable developments have been made concerning the chemistry and catalytic application of oxidomolybdenum complexes. It has been shown that the Mo^V oxido-bridged dinuclear complexes [Mo₂O₂(µ₂-O)Cl₄(di $tBu-bipy_2$ (3) and $[Mo_2O_2(\mu_2-O)_2Cl_2(di-tBu-bipy)_2]$ (4) can be isolated in good yields by treatment of the Mo^{VI} complex [MoO₂Cl₂(di-tBu-bipy)] (1) with the alcohols ethanol and 1-phenylethanol, which function simultaneously as reducing agents and solvents. In the presence of ethanol, the Mo^{VI} oxidoalkoxido complex [MoO2Cl(OEt)(di-tBu-bipy)] (2) was also isolated and structurally characterised. The formation of this complex is significant from a number of viewpoints. To the best of our knowledge, it is the first example of a mixedligand complex of the type $[MoO_2X(OR)(L)]$, where X = halide or alkyl group. From a structural perspective the complex is remarkable in presenting an all-cis configuration rather than the far more common cis-oxido, trans-X, cis-L configuration normally exhibited by complexes of the type $[MoO_2X_2(L)]$. The complex could, in principle, be an intermediate in the conversion of 1 to 3, a pathway that would have clear parallels with that generally presented for the oxidation of ethanol to acetaldehyde over supported molybdenum oxide catalysts. Indeed, complex 2 can be viewed as a valuable model compound for the latter catalytic process.

To date, catalytic studies with complexes of the type $[MoO_2X_2(L)]$ (L = bidentate organic ligand) have essentially been limited to liquid-phase olefin epoxidation using alkylhydroperoxides as oxidants. In the present work, complex 1 was studied as a (pre)catalyst in acid-catalysed reactions performed under mild conditions, namely the acetalisation of benzaldehyde and the ethanolysis of styrene oxide. Good results were obtained for both reactions with selective formation of the target products benzaldehyde diethyl acetal and 2-ethoxy-2-phenylethanol. Whereas complex 1 appears to be essentially the active species responsible for the acetalisation reaction, in the presence of styrene oxide the complex undergoes a transformation to the octanuclear complex $[Mo_8O_{24}(di-tBu-bipy)_4]$ (6). In separate assays, complex 6 was shown to catalyse the ethanolysis of styrene oxide with high activity and selectivity, and could be recovered unchanged at the end of the reaction.

In future work we plan to further study the catalytic performance of 6 and related oxidomolybdenum complexes in other acid-catalysed organic transformations. The impact of known and as yet undiscovered oxidomolybdenum complexes in the field of acid catalysis may supersede that of oxidation catalysis for which they have been essentially investigated to date.

Experimental section

General procedures and materials

Solvents were dried by standard procedures, distilled under nitrogen and stored over 4 Å molecular sieves. MoO_2Cl_2 , 4,4'-ditert-butyl-2,2'-bipyridine, hexane (99%), pentane (99%), acetone (99.5%), diethyl ether (99.8%), styrene oxide (98%), benzaldehyde (\geq 99%), 1-phenylethanol (>98%), 2-phenylethanol (>98%), 1-octene (98%), and nonane (99%) were purchased from Sigma-Aldrich and used as received. Anhydrous absolute ethanol (99.9%) was acquired from Carlo Erba and used as received. The complexes [$MoO_2Cl_2(di-tBu-bipy)$] (1) and [$Mo_8O_{24}(di-tBu-bipy)_4$] (6) were prepared as described previously.^{9a,e} The large-scale contact tests were performed under nitrogen.

Elemental analysis for C, H, and N was performed by M. Marques at the University of Aveiro with a Leco TruSpec 630-200-200 analyser. PXRD data were collected at ambient temperature using a PANalytical Empyrean instrument equipped with a PIXcel 1D detector set at 240 mm from the sample. Cu-K_{α 1,2} X-radiation (λ_1 = 1.540598 Å; λ_2 = 1.544426 Å) filtered with a nickel foil was used along with a standard reflection sample holder. Working operating conditions for the X-ray tube: 45 kV and 40 mA. Intensity data were collected in continuous mode in the *ca.* 3.5 $\leq 2\theta \leq$ 70° range.

Transmission FT-IR spectra were measured as KBr pellets on a Unican Mattson 7000 spectrophotometer equipped with a DTGS CsI detector (resolution 4 cm⁻¹, 128 scans). 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 (resolution 4 cm⁻¹, 256 scans). ¹H NMR spectra in solution were recorded using a Bruker CPX 300 spectrometer at ambient temperature. Chemical shifts are given in ppm relative to tetramethylsilane.

Large-scale contact tests (LSCT)

Complex 1, ethanol, reflux/24 h. A mixture comprising the mononuclear complex 1 (0.50 g, 1.07 mmol) and anhydrous ethanol (40 mL) was heated under reflux for 24 h. The resultant bordeaux coloured precipitate was filtered, washed with ethanol (3 × 20 mL), pentane (3 × 20 mL), and diethyl ether (3 × 20 mL), and finally vacuum-dried to give the molybdenum(v) dinuclear complex $[Mo_2O_2(\mu_2-O)Cl_4(di-tBu-bipy)_2]$ (3) (0.31 g, 63%). Anal. calcd for $C_{36}H_{48}Cl_4Mo_2N_4O_3$ (918.48): C, 47.08; H, 5.27; N, 6.10. Found: C, 46.95; H, 5.41; N, 5.95. FT-IR (KBr, cm⁻¹): v = 2960 (m), 2908 (w), 2870 (w),

1617 (vs), 1544 (m), 1486 (m), 1467 (sh), 1413 (s), 1369 (m), 1307 (w), 1251 (m), 1203 (m), 1122 (w), 1081 (w), 1031 (sh), 1022 (m), 964 (vs), 902 (m), 840 (s), 786 (m), 740 (w), 717 (w), 605 (m), 551 (w), 447 (m), 320 (m). ¹H NMR (300 MHz, CD₃COCD₃): δ = 9.12 (d, 2H, H^{6/6'}, ³J_{H-H} = 6 Hz), 8.92 (d, 2H, H^{6/6'}, ³J_{H-H} = 6 Hz), 8.67 (d, 2H, H^{3/3'}, ⁴J_{H-H} = 2 Hz), 8.61 (d, 2H, H^{3/3'}, ⁴J_{H-H} = 2 Hz), 7.80 (dd, 2H, H^{5/5'}, ³J_{H-H} = 6 Hz, ⁴J_{H-H} = 2 Hz), 7.75 (dd, 2H, H^{5/5'}, ³J_{H-H} = 6 Hz, ⁴J_{H-H} = 2 Hz), 1.52 (s, 18H, C(CH₃)₃), 1.44 (s, 18H, C(CH₃)₃).

After the reaction of 1 in ethanol, the filtrate (mother liquor) was subjected to vapour diffusion by pentane, which gave small crops of vellow crystals of the Mo^{VI} oxidoalkoxido complex [MoO₂Cl(OEt)(di-tBu-bipy)] (2) and orange crystals of the Mo^V dinuclear complex $[Mo_2O_2(\mu_2-O)_2Cl_2(di-tBu-bipy)_2]$ ·2EtOH (4·2EtOH). These were mechanically separated and found to be suitable for structure determination by X-ray diffraction. In addition to these crystals, a small amount of bordeaux precipitate (0.08 g) was obtained, which was identified as a mixture comprising complexes 1 (ca. 10 mol%), 2 (ca. 80 mol%) and 3 (ca. 10 mol%) by ¹H NMR and PXRD (combined vield of 15% based on Mo): characterisation data for 2: Anal. calcd for C₂₀H₂₉ClMoN₂O₃ (476.84): C, 50.38; H, 6.13; N, 5.87. Found: C, 50.33; H, 5.76; N, 5.76. FT-IR (KBr, cm^{-1}): v = 2968(m), 2908 (w), 2869 (w), 1614 (s), 1548 (m), 1486 (m), 1465 (m), 1409 (s), 1365 (m), 1307 (w), 1252 (m), 1203 (w), 1160 (w), 1122 (w), 1089 (w), 1057 (s), 1032 (m), 931 (m), 905 (vs), 889 (s), 865 (m), 750 (w), 737 (w), 721 (w), 607 (m), 553 (w), 482 (w), 404 (w), 376 (w), 343 (w). ¹H NMR (300 MHz, CDCl₃):
$$\begin{split} &\delta = 8.99 \; (\text{d}, \, 2\text{H}, \, \text{H}^{6/6'}, \, {}^{3}\!\!J_{\text{H}-\text{H}} = 6 \; \text{Hz}), \, 8.14 \; (\text{d}, \, 2\text{H}, \, \text{H}^{3/3'}, \, {}^{4}\!\!J_{\text{H}-\text{H}} = 2 \\ &\text{Hz}), \, 7.54 \; (\text{dd}, \, 2\text{H}, \, \text{H}^{5/5'}, \, {}^{3}\!\!J_{\text{H}-\text{H}} = 6 \; \text{Hz}, \, {}^{4}\!\!J_{\text{H}-\text{H}} = 2 \; \text{Hz}), \, 3.72 \; (\text{q}, \, \text{Hz}) \; \text{Hz} = 0 \; \text{Hz}, \, 100 \; \text{Hz}$$
2H, OCH₂CH₃, ${}^{3}J_{H-H}$ = 7 Hz), 1.48 (s, 18H, C(CH₃)₃), 1.24 (t, 3H, OCH₂CH₃, ${}^{3}J_{H-H} = 7$ Hz).

Complex 1, 1-phenylethanol, 130 °C. A mixture comprising the mononuclear complex 1 (0.50 g, 1.07 mmol) and 1-phenylethanol (20 mL) was heated at 130 °C for 24 h. A dark red-orange solution was obtained. Addition of pentane (40 mL) resulted in the precipitation of an orange solid, which was filtered, washed with pentane $(3 \times 20 \text{ mL})$ and diethyl ether (3 \times 20 mL), and finally vacuum-dried to give the molybdenum(v) dinuclear complex $[Mo_2O_2(\mu_2-O)_2Cl_2(di$ $tBu-bipy_{2}$ (4) in 73% yield (0.34 g). Anal. calcd for C₃₆H₄₈Cl₂Mo₂N₄O₄ (863.57): C, 50.07; H, 5.60; N, 6.49. Found: C, 49.75; H, 5.51; N, 6.25. FT-IR (KBr, cm^{-1}): v = 2964 (m), 2908 (w), 2871 (w), 1616 (vs), 1547 (m), 1486 (m), 1465 (w), 1412 (s), 1367 (m), 1305 (w), 1292 (w), 1251 (m), 1201 (w), 1157 (w), 1124 (w), 1082 (w), 1027 (m), 956 (vs), 935 (sh), 900 (m), 848 (m), 728 (m), 606 (m), 551 (w), 485 (m). ¹H NMR (300 MHz, CDCl₃): δ = 9.88 (d, 2H, H^{6/6'}, ${}^{3}J_{H-H}$ = 6 Hz), 8.24 (d, 2H, $H^{3/3'}$, ${}^{4}J_{H-H}$ = 2 Hz), 8.04 (d, 2H, $H^{3/3'}$, ${}^{4}J_{H-H}$ = 2 Hz), 7.80 (dd, 2H, $H^{5/5'}$, ${}^{3}J_{H-H} = 6$ Hz, ${}^{4}J_{H-H} = 2$ Hz), 7.35 (d, 2H, $H^{6/6'}$, ${}^{3}J_{H-H} = 6$ Hz), 6.67 (dd, 2H, H^{5/5'}, ${}^{3}J_{H-H} = 6$ Hz, ${}^{4}J_{H-H} = 2$ Hz), 1.57 (s, 18H, C(CH₃)₃), 1.38 (s, 18H, C(CH₃)₃).

Recrystallisation of 4 from chloroform/hexane (liquid-liquid slow diffusion) resulted in orange crystals of $[Mo_2O_2(\mu_2-O)_2Cl_2(di-tBu-bipy)_2]$ -5CHCl₃ (4-5CHCl₃) suitable for structure determination by X-ray diffraction. **Complex 1,** *tert*-butanol, reflux. A mixture comprising the mononuclear complex 1 (0.15 g, 0.32 mmol) and *tert*-butanol (15 mL) was stirred under reflux for 24 h, and then filtered to separate the resultant pink-coloured solution from unreacted 1. Addition of pentane (20 mL) to the filtrate gave a pink precipitate, which was filtered, washed with pentane (3 × 10 mL), vacuum-dried, and identified as the molybdenum(vi) oxidobridged dinuclear complex $[Mo_2O_4(\mu_2-O)Cl_2(di-tBu-bipy)_2]$ (5) (10 mg, 7%) by FT-IR spectroscopy and PXRD.

Single-crystal X-ray diffraction studies

Crystalline material of the compounds [MoO2Cl(OEt)(di-tBubipy)] (2), $[Mo_2O_2(\mu_2-O)_2Cl_2(di-tBu-bipy)_2]\cdot 2EtOH$ (4·2EtOH) and $[Mo_2O_2(\mu_2-O)_2Cl_2(di-tBu-bipy)_2]$ ·5CHCl₃ (4·5CHCl₃) were collected from the crystallisation vials and immediately immersed in highly viscous FOMBLIN Y perfluoropolyether vacuum oil (LVAC 140/13, Sigma-Aldrich). Selected single-crystals of each compound were mounted on CryoLoops with the assistance of a stereomicroscope.³¹ Diffraction data sets were obtained at 150(2) K on a Bruker X8 APEX II CCD areadetector diffractometer (Mo K_{α} graphite-monochromated radiation, $\lambda = 0.71073$ Å) controlled by the APEX2 software package,³² and equipped with an Oxford Cryosystems Series 700 cryostream. Images were processed using the software package SAINT+,33 and the absorption effects were corrected by the multi-scan semi-empirical method implemented in SADABS.³⁴ The structures were solved using the algorithms implemented in SHELXT-2014,35,36 allowing the direct location of most of the heaviest atoms. The remaining non-H atoms were located from difference Fourier maps calculated from successive full-matrix least squares refinement cycles on F^2 using SHELXL-v.2014,^{35,37} and all of them were successfully refined using anisotropic displacement parameters.

H-atoms bound to carbon were located at model geometrical positions using suitable HFIX instructions in SHELXL: 43 for the aromatic, 13 for ==CH-, 23 for -CH₂- and 137 for the terminal -CH₃ methyl groups belonging to the di-tBu-bipy and OEt ligands, as well as to the solvent molecules of crystallisation, EtOH and CHCl₃. All of these atoms were included in subsequent refinement cycles in riding-motion approximation with isotropic thermal displacement parameters $(U_{\rm iso})$ fixed at 1.2 (aromatic, =CH- and -CH₂- groups) or 1.5 (-CH₃ groups) times U_{eq} of the attached carbon atom. In 4.2EtOH, the H-atoms of the OH groups in the EtOH molecules of crystallisation were clearly visible in the difference Fourier maps, included in the final structure model during subsequent refinement stages with the O-H distances restrained to 0.95(1), and further treated by a riding-motion approximation with an isotropic thermal displacement parameter (U_{iso}) fixed at 1.5 \times U_{eq} of the parent oxygen atom. In the structure of compound 2, a central {MoO2Cl} group is disordered over two positions with occupancy factors of 15% and 85%. Table S1 (ESI[†]) summarises relevant information about the crystal data, single-crystal X-ray data collection and structure refinement details of 2, 4.2EtOH and 4.5CHCl₃.

Catalytic tests

The reactions were carried out with magnetic stirring (1000 rpm), under air, in closed borosilicate micro-reactors (5 mL) equipped with a valve to allow sampling. Typically, the reactor was charged with (pre)catalyst (equivalent to 20 μ mol of Mo), substrate (0.4 mmol) and ethanol (1 mL), and immersed in a temperature-controlled oil bath.

The reaction mixtures were analysed by using a Varian 3900 GC equipped with a DB-5 capillary column (30 m \times 0.25 mm \times 0.25 μ m) and a FID detector, with H₂ as the carrier gas. 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. 1-Octene and nonane were used as internal standards added after the reaction for the substrates styrene oxide and benzaldehyde, respectively.

After a batch run, the reaction mixture was cooled to ambient temperature and the undissolved solid was separated from the liquid phase by centrifugation (3500 rpm), washed with pentane, and vacuum-dried (ca. 0.1 bar) at 55 °C for 1 h. The liquid phase was filtered through a 0.2 µm PTFE membrane and, after addition of pentane, stored at 4 °C overnight. Any resultant precipitate was separated by centrifugation (3500 rpm), washed with pentane or diethyl ether, and vacuum-dried (ca. 0.1 bar) at 55 °C for 1 h. Contact tests (CT) were carried out for different complexes as follows: a mixture of complex and alcohol solvent was stirred at 55 °C for 24 h. Afterwards, the mixture was cooled to ambient temperature, centrifuged (3500 rpm), and the dissolved (denoted 1/CT-liq) and undissolved (1/CT-sol) metal species were isolated as described above for the normal catalytic batch runs. The recovered solids were characterised by ATR FT-IR spectroscopy and PXRD.

Acknowledgements

We acknowledge funding by FEDER (Fundo Europeu de Desenvolvimento Regional) through COMPETE (Programa Operacional Factores de Competitividade). National funding through the FCT (Fundação para a Ciência e a Tecnologia) within the project FCOMP-01-0124-FEDER-029779 (FCT ref. PTDC/QEQ-SUP/1906/2012, including the research grant with ref. BPD/UI89/4864/2014 to A. C. G.) is thanked. This work was developed in the scope of the projects CICECO - Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT ref. UID/CTM/50011/2013), and REQUIMTE-LAQV (UID/QUI/ 50006/2013), financed by national funds through the FCT/ MEC and co-financed by FEDER under the PT2020 Partnership Agreement. The FCT and the European Union are acknowledged for post-doctoral grants to A. C. G. (SFRH/BPD/ 108541/2015) and P. N. (SFRH/BPD/73540/2010) co-funded by MCTES and the European Social Fund through the program POPH of QREN. The FCT and CICECO are acknowledged for financial support toward the purchase of the single-crystal diffractometer.

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