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Molybdenum(II) Diiodo-Tricarbonyl Complexes Containing Nitrogen Donor Ligands as Catalyst Precursors for the Epoxidation of Methyl Oleate

Carla A. Gamelas · Patrícia Neves · Ana C. Gomes · Anabela A. Valente · Carlos C. Romão · Isabel S. Gonçalves · Martyn Pillinger

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Abstract The molybdenum(II) tricarbonyl complexes $[Mo(CO)_3I_2L_n]$ ($n = 1$, L = 2,2′-bipyridine, 4,4′-di-*tert*-butyl-2,2′-bipyridine; $n = 2$, L = pyridine, 4-*tert*-butylpyridine) have been examined as catalyst precursors for the epoxidation of the biorenewable olefin methyl oleate with *tert*-butylhydroperoxide. In situ oxidative decarbonylation of the precursors gives highly active and selective molybdenum(VI) catalysts, which were identified as the one-dimensional molybdenum oxide/bipyridine polymer $[MoO_3(2,2'\text{-bipyridine})]$, octanuclear $[Mo_8O_{24}(4,4'\text{-di-}tert\text{-butyl-}2,2'\text{-bipyridine})_4]$, and the pyridinium β-octamolybdates $(LH)_4[Mo_8O_{26}]$ for L = pyridine or 4-*tert*-butylpyridine.

Keywords Molybdenum · Oxidative decarbonylation · Alkenes · Epoxidation · *tert*-butylhydroperoxide · Methyl oleate · Biomass conversion

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C. A. Gamelas · C. C. Romão
Instituto de Tecnologia Química e Biológica da Universidade
Nova de Lisboa, Av. da República, Estação Agronómica
Nacional, 2780-157 Oeiras, Portugal

C. A. Gamelas
Escola Superior de Tecnologia, Instituto Politécnico de Setúbal,
2910-761 Setúbal, Portugal

P. Neves · A. C. Gomes · A. A. Valente ·
I. S. Gonçalves (✉) · M. Pillinger (✉)
Department of Chemistry, CICECO, University of Aveiro,
3810-193 Aveiro, Portugal
e-mail: igoncalves@ua.pt

M. Pillinger
e-mail: mpillinger@ua.pt

1 Introduction

The use of molybdenum carbonyl complexes as precursors to molybdenum(VI) catalysts for the epoxidation of olefins has been intensively researched since 2003, when Abrantes et al. [1] reported that highly active $(\eta^5\text{-}C_5R_5)MoO_2Cl$ catalysts (R = H, CH_3, CH_2Ph) could be generated in situ by reaction of the tricarbonyl complexes $(\eta^5\text{-}C_5R_5)Mo(CO)_3Cl$ with the oxidant *tert*-butylhydroperoxide (TBHP). In the following years various cyclopentadienyl molybdenum complexes of the type $Cp'Mo(CO)_3X$ ($Cp' = \eta^5\text{-}C_5R_5$, $\eta^5\text{-}C_5H_4R$, $\eta^5\text{-}C_9H_7$; X = halide, alkyl) [2–11], $Cp^xMo(CO)_3$ and $Cp^xMo(CO)_2X$ (Cp^x = cyclopentadienyl functionalized with cycloalkyl, N-heterocyclic carbene (NHC), oxazoline, or diphenyl phosphine moieties as bridging units) [12–17], $Cp'Mo(CO)_2(\eta^3\text{-allyl})$ [18], and $CpMo(CO)_2(NHC)X$ [19] have been investigated. The molybdenum(VI) species formed upon oxidative decarbonylation of these precursors include $Cp'MoO_2X$, $Cp'MoO(O_2)X$, $[Cp'MoO_2]_2(\mu\text{-O})$ and $[Cp'MoO(O_2)]_2(\mu\text{-O})$ from $Cp'Mo(CO)_3X$, and $[CpMoO_2(NHC)]BF_4$ from $[CpMo(CO)_2(NHC)(NCMe)](BF_4)$. Besides these cyclopentadienyl complexes, several other types of molybdenum carbonyl complexes have been studied, including the η^3-allyl dicarbonyl complexes $[Mo(\eta^3\text{-allyl})Cl(CO)_2(\text{bis-NHC})]$ [20] and $[Mo(\eta^3\text{-allyl})Cl(CO)_2(L)]$ [21, 22], heptacoordinate tricarbonyl complexes $[Mo(CO)_3I_2(L)]$ [23], and the tetracarbonyl complexes *cis*-$[Mo(CO)_4(L)]$ [24–26] (L is a bidentate chelating dinitrogen ligand such as diazabutadiene, bipyridine, pyridylimine or pyrazolylpyridine). Due to the structure-directing influence of the organodiamine ligand, oxidative decarbonylation of these complexes leads to a diverse range of molybdenum(VI) species with different catalytic performances. Some of the species formed include tetranuclear $[Mo_4O_{12}L_4]$ for L = 2-[3(5)-pyrazolyl]pyridine [25], octanuclear $[Mo_8O_{24}L_4]$ for L = 4,4′-di-*tert*-butyl-2,2′-bipyridine (di-tBu-bipy) [22, 24] and ethyl[3-(2-pyridyl)-1-pyrazolyl]acetate [25], and the one-dimensional molybdenum oxide/bipyridine polymer [MoO_3L] for L = 2,2′-bipyridine (bipy) [24].

Despite the promising results obtained with the catalytic systems mentioned above, there is room for further work in the field of selective epoxidation catalysis, with one of the most interesting aims being the development of efficient systems for the epoxidation of biorenewable olefins [27]. Of particular interest are plant derived olefins such as (*R*)-(+)-limonene, α-pinene, and fatty acids and esters obtained from vegetable oils [27–29]. In industry, epoxidized vegetable oils (EVO) are currently mainly used as plasticizers and stabilizers for polyvinyl chloride (PVC) plastics [30–33]. Other potential uses of EVOs are as lubricant and anti-rust additives [34–40], in UV-curable coatings [41–46], and as raw materials for the synthesis of a broad variety of polymeric materials [47, 48]. For example, oxirane ring opening of EVOs by reaction with alcohols can give polyols, which are intermediates for the production of lubricants and polyurethanes [49, 50]. EVOs are commercially produced via the Prileshajev peracid process [29]. However, this process has several drawbacks, such as low selectivity to epoxidized products due to the acid-catalyzed oxirane ring opening, the need to use excess H_2O_2 and long reaction times, and corrosion problems due to the presence of a strong acid in an oxidative environment. The use of transition metal complexes as epoxidation catalysts may eliminate many of these problems and permit highly selective reactions [29]. To this end, molybdenum-based catalytic systems have been successfully investigated, such as [MoO_2(SAP)(EtOH)] (SAP = dianionic tridentate salicylideneiminophenolate chelating ligand) plus organic hydroperoxides for the epoxidation of oleic acid [51], [$MoO(O_2)_2$(8-quinolinol)$_2$] plus $H_2O_2/NaHCO_3$ for the epoxidation of a mixture of methyl oleate (MO) and methyl linoleate [52], [$MoO_2(acac)_2$] plus TBHP for the epoxidation of soybean oil [53], and the octanuclear complex [$Mo_8O_{22}(OH)_4$(di-tBu-bipy)$_4$] plus TBHP for the epoxidation of MO [54].

As part of our ongoing exploration of molybdenum carbonyl complexes as catalyst precursors for the epoxidation of bio-derived olefins, we now wish to report on the use of the heptacoordinate molybdenum(II) tricarbonyl complexes [$Mo(CO)_3I_2L_n$] ($n = 1$, L = bipy, di-tBu-bipy; $n = 2$, L = pyridine, 4-*tert*-butylpyridine) in the catalytic epoxidation of MO using TBHP as oxidant.

2 Experimental

2.1 Materials and Methods

Microanalyses for CHN were performed at the ITQB (by C. Almeida) and ICP-OES were performed at the University of Aveiro (by L. Carvalho). ^1H, $^{13}C\{^1H\}$, ^1H–^1H COSY and ^1H–^{13}C HMQC NMR spectra were recorded at room temperature on a Bruker Avance II 400 MHz spectrometer. Chemical shifts (δ) are quoted in parts per million from tetramethylsilane. Transmission FT-IR spectra were measured on a Mattson 7000 FT-IR spectrometer using KBr pellets. Attenuated total reflectance (ATR) FT-IR spectra were measured on a Bruker optics Tensor 27 equipped with a Specac Golden Gate Mk II ATR accessory having a diamond top-plate and KRS-5 focusing lenses.

All air-sensitive operations were carried out using standard Schlenk techniques under nitrogen. Solvents were dried by standard procedures, distilled under nitrogen and kept over molecular sieves. Pyridine (py), 4-*tert*-butylpyridine (tBu-py), 2,2′-bipyridine (bipy), 4,4′-di-*tert*-butyl-2,2′-bipyridine (di-tBu-bipy), and *tert*-butylhydroperoxide (TBHP, 5–6 M in decane) were obtained from Sigma-Aldrich and used as received. [$Mo(CO)_3I_2(NCMe)_2$] [55], [$Mo(CO)_3I_2(bipy)_2$] (**1**) and [$Mo(CO)_3I_2(py)_2$] (**3**) [56] were prepared by following literature procedures, and presented satisfactory infrared and NMR data: For **1**, ν(CO) = 2030vs, 1969vs, 1913vs cm^{-1}; ^1H NMR (CD_3COCD_3) $\delta = 9.32$ (d, 2H, H6,6′ bipy), 8.67 (d, 2H, H3,3′ bipy), 8.24 (td, 2H, H4,4′ bipy), 7.70 (t, 2H, H5,5′ bipy); $^{13}C\{^1H\}$ NMR (CD_3COCD_3) $\delta = 233.8$ (CO), 157.6 (C2,2′ and C6,6′ bipy), 141.5 (C4,4′ bipy), 127.9 (C5,5′ bipy), 125.6 (C3,3′ bipy). For **3**, ν(CO) = 2016s, 1998vs, 1939s, 1921vs, 1869sh; ^1H NMR (DMSO-d_6) $\delta = 8.76$ (br, 4H, H2 py), 8.16 (br, 2H, H4 py), 7.71 (br, 4H, H3 py); $^{13}C\{^1H\}$ NMR (DMSO-d_6) $\delta = 147.0$ (C2 py), 139.8 (C4 py), 125.1 (C3 py). [$Mo(CO)_3I_2$(di-tBu-bipy)] (**2**) was prepared by addition of a freshly dried solution of di-tBu-bipy (0.25 g, 0.93 mmol) in ethanol to a solution of [$Mo(CO)_3I_2(NCMe)_2$] (0.48 g, 0.93 mmol) in ethanol. The reaction mixture was stirred at room temperature for 90 min in the dark. After concentration and addition of diethyl ether/*n*-hexane, the resultant yellow precipitate was filtered, washed with diethyl ether and *n*-hexane, and finally vacuum dried (0.56 g, 85 %). NMR and FT-IR spectra for **2** were in agreement with literature data [57].

2.2 Preparation of [$Mo(CO)_3I_2$(tBu-py)$_2$] (**4**)

*t*Bu-py (0.16 mL, 1.06 mmol) was added to a solution of [$Mo(CO)_3I_2(NCMe)_2$] (0.27 g, 0.53 mmol) in dichloromethane, and the reaction mixture was stirred at room temperature for 20 min in the dark. After removal of the solvent under reduced pressure, the resultant light brown solid was washed with diethyl ether and finally vacuum dried (0.30 g, 81 %). Anal. Calcd. for $C_{21}H_{26}I_2MoN_2O_3$: C, 35.82; H, 3.72; N, 3.98. Found: C, 35.70; H, 3.76; N, 3.94 %. FT-IR (KBr, cm^{-1}): ν(CO) 2013vs, 1944vs, 1911vs. ^{1}H NMR (DMSO-d$_6$): $\delta = 8.73$ (br, 4H, H2 py), 7.87 (br, 4H, H3 py), 1.33 (s, 18H, CMe$_3$). ^{13}C{^{1}H} NMR (DMSO-d$_6$): $\delta = 213.9$ (CO), 204.3 (CO), 167.6 (C4 py), 143.7 (C2 py), 124.2 (C3 py), 35.7 (*C*Me$_3$), 29.7 (C*Me*$_3$).

2.3 Catalytic Epoxidation of MO

The reactions of MO (99 %, Sigma-Aldrich) with TBHP were carried out at 75 °C in batch borosilicate micro reactors (5 mL capacity), under magnetic stirring (1,000 rpm). The initial molar ratios of molybdenum:olefin:oxidant were 1:100:152 (18 μmol Mo), and 1 mL of 1,2-dichloroethane (DCE, 99 %, Sigma-Aldrich) or 0.3 mL of the ionic liquid (IL) 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF$_4$, Merck) were used as cosolvent. The acquired cosolvents and oxidant solution were dried prior to the catalytic tests: DCE was treated with CaH$_2$ at room temperature overnight with stirring, followed by distillation and storage over activated 4 Å molecular sieves; [bmim]BF$_4$ was treated at 100 °C under vacuum for 2 h; TBHP was dried using activated 3 Å molecular sieves. The reactors were charged with MO and cosolvent and immersed in a thermostated oil bath (at 75 °C) for 10 min, followed by addition of TBHP (which was pre-heated at the reaction temperature). It is considered that the catalytic reaction began at the instant that TBHP was added to the reactor. The course of the reactions was monitored by GC using a Varian V3800 equipped with a BR-5 capillary column (30 m × 0.25 mm × 0.25 μm). Methyl decanoate was used as internal standard. The reaction products were identified by GC–MS (Trace GC 2000 Series Thermo Quest CE Instruments GC; Thermo Scientific DSQ II) using He as carrier gas.

2.4 Isolation of Oxidized Metal Compounds **1*–4***

Reactions were carried out as described in Sect. 2.3 (with DCE as cosolvent), but on a larger scale and without MO. After 24 h the reaction mixtures were concentrated, diethyl ether added, and the resultant solids isolated by filtration, washed with CH$_2$Cl$_2$, *n*-hexane and diethyl ether, and finally vacuum-dried. FT-IR data for **1*** (obtained from **1**) and **2*** (obtained from **2**) were in agreement with published data for the molybdenum oxide/bipyridine polymer [MoO$_3$(bipy)] and the octanuclear complex [Mo$_8$O$_{24}$(di-tBu-bipy)$_4$], respectively [24]. Compounds **3*** (obtained from **3**) and **4*** (obtained from **4**) were identified as the pyridinium *β*-octamolybdates (C$_5$H$_5$NH)$_4$[Mo$_8$O$_{26}$] and [(CH$_3$)$_3$CC$_5$H$_4$NH]$_4$[Mo$_8$O$_{26}$], respectively, on the basis of elemental analyses, FT-IR spectra, and NMR data.

Data for **3*** Anal. Calcd. for $C_{20}H_{24}Mo_8N_4O_{26}$: C, 15.97; H, 1.61; N, 3.72. Found: C, 16.20; H, 1.36; N, 3.59 %. FT-IR (KBr, cm^{-1}): $v = 3107$w, 3069w, 2963w, 2927w, 2360w, 2341w, 1633m, 1609sh, 1532w, 1486m, 1475m, 1261m, 1204w, 1097m, 1027m, 946s, 912s, 839m, 802m, 709s, 675s, 554w, 523w. ^{1}H NMR (DMSO-*d*$_6$): $\delta = 8.66$ (br, 8H, H2 py), 7.97 (t, 4H, H4 py), 7.54 (dd, 8H, H3 py).

Data for **4*** Anal. Calcd. for $C_{36}H_{56}Mo_8N_4O_{26}$: C, 25.02; H, 3.27; N, 3.24. Found: C, 25.50; H, 3.46; N, 3.00 %. FT-IR (KBr, cm^{-1}): $v = 3263$w, 3083w, 2964m, 2928m, 2358w, 2339w, 1635m, 1597w, 1500w, 1463w, 1375w, 1263w, 1211w, 1102w, 1023w, 949s, 914m, 837m, 799s, 708m, 659m, 559w, 525w. ^{1}H NMR (DMSO-*d*$_6$): $\delta = 8.68$ (br, 8H, H2 py), 7.74 (d, 8H, H3 py), 1.38 (s, 36H, CMe$_3$).

3 Results and Discussion

3.1 Preparation of Catalyst Precursors

The complexes [Mo(CO)$_3$I$_2$L$_n$] ($n = 1$, L = bipy (**1**), di-tBu-bipy (**2**); $n = 2$, L = pyridine (**3**), 4-*tert*-butylpyridine (**4**)) (Chart 1) were readily prepared in very good yields by replacement of the acetonitrile ligands in [Mo(CO)$_3$I$_2$(NCMe)$_2$] by the nitrogen donor ligands. Since the bis-acetonitrile complex can be synthesized in excellent yield from Mo(CO)$_6$ by reaction with MeCN to give [Mo(CO)$_3$(NCMe)$_3$] followed by reaction with I$_2$, complexes **1**–**4** are potentially interesting as catalyst precursors due to their easy preparation from cheap starting materials [58]. To the best of our knowledge, the 4-*tert*-butylpyridine (tBu-py) complex **4** has not been previously reported. The FT-IR spectrum of **4** measured in KBr pellets shows three very strong *v*(CO) bands at 2013, 1944 and 1911 cm^{-1} typical of complexes of the type [Mo(CO)$_3$I$_2$L$_n$]. Coordination of the tBu-py ligand is indicated by the shift of the pyridyl ring stretching vibration from 1,597 cm^{-1} for the free ligand to 1,619 cm^{-1} for **4**. The ^{1}H NMR spectrum of **4** (25 °C, DMSO-d$_6$) shows the expected two broad signals at δ 8.73 and 7.87 for the pyridine protons, and a singlet at δ 1.33 for the methyl groups.

3.2 Catalytic Epoxidation of MO

The reaction of MO with TBHP at 75 °C using complexes **1**–**4** as catalyst precursors and a Mo:MO:TBHP molar ratio of 1:100:152 gave methyl 9,10-epoxystearate (MES) as the main product in up to 71 % yield at ca. 80 % conversion, 24 h (Scheme 1). No MES was formed in the absence of catalyst precursor. By-products included methyl-9,10-dihydroxyoctadecanoate, which may be formed via hydrolysis of MES with adventitious water present in the reaction mixture (since the substrate was not pre-dried and the catalytic reactions were carried out under atmospheric air), and other non-identified compounds. The dependence of MES yield on MO conversion was comparable for **1**/**2** (58–62 % yield at 65–72 % conversion) and 3/4 (16 % yield at ca. 25 % conversion), Fig. 1. However,

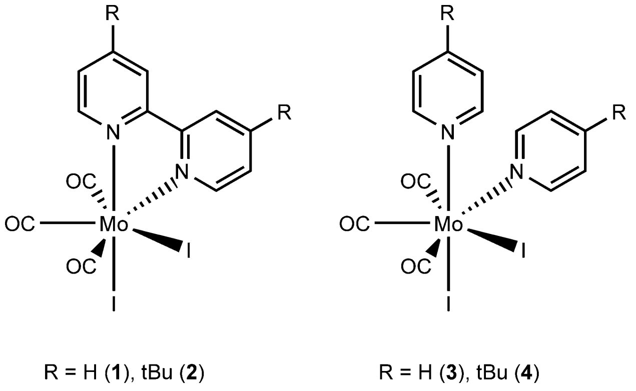
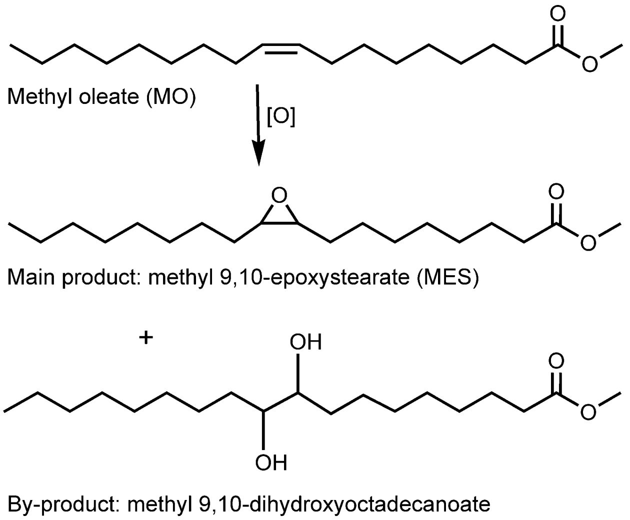


Chart 1 Catalyst precursors used in this work

considerable differences in reaction rate (based on conversions at 6, 24 h) were observed for **1**–**4**, following the order **2** (65, 78 %) > **1** (47, 72 %) >> **4** (23, 37 %) > **3** (16, 25 %) (Fig. 1). A comparison of **1**/**2** and **3**/**4** suggests that the introduction of the *tert*-butyl substituents in the aromatic ligands enhances the reaction rate. A similar effect has been reported in the literature for molybdenum tetracarbonyl complexes of the type *cis*-[$Mo(CO)_4(L)$], where L is bipy or di-tBu-bipy, tested as catalyst precursors in the epoxidation of *cis*-cyclooctene with TBHP; the complex with L = di-tBu-bipy was more soluble and led to a faster catalytic reaction [24]. Complex **2** is apparently more soluble than the other three complexes, which may account for faster in situ formation of the active species, enhancing the overall reaction rate of MO.

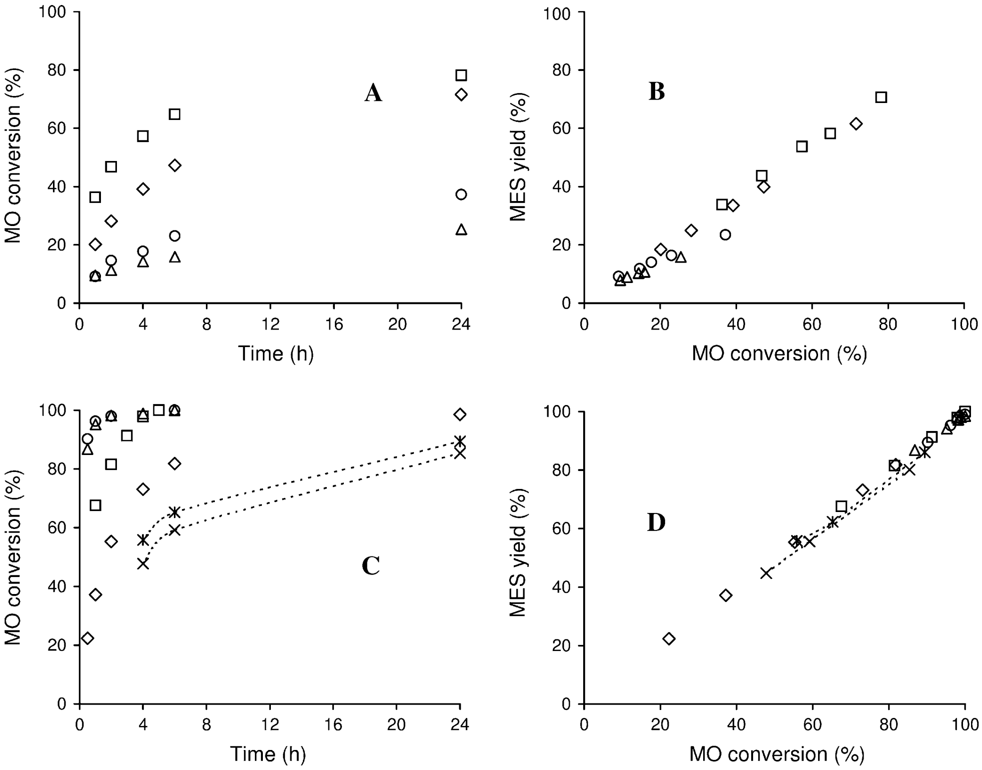
The complexes bearing bidentate ligands (**1** and **2**) lead to enhanced reaction rates in comparison to those possessing the corresponding monodentate ligands (**3** and **4**, respectively), Fig. 1. These results may be at least partly related with the different types (and properties) of the active species formed and/or their rates of formation. The transformation of the precursor complexes was evidenced by color changes in the reaction mixtures after addition of TBHP. In the few reports dealing with complexes of the type [$Mo(CO)_3X_2L_n$] (X = Br, I; $n = 1$ or 2 for L = bidentate or monodentate ligand, respectively) used as catalyst precursors for liquid-phase epoxidation of olefins with TBHP [23, 59, 60], the oxidized metal compounds were not identified. In the present work, the oxidized metal compounds could be isolated by scaling up the catalytic experiments. The FT-IR spectra of all four compounds (**1***, **2***, **3*** and **4*** from **1**, **2**, **3** and **4**) show the absence of ν(CO) bands (Fig. 2). For **1*** and **2***, the spectra match those reported previously for the compounds [MoO_3(bipy)] and [Mo_8O_{24}(di-tBu-bipy)$_4$], respectively [22, 24]. In addition to bands due to bipy or di-tBu-bipy, the spectra exhibit several bands in the range of 600–950 cm^{-1} due to Mo–O vibrations. The characteristic bands are found at 622, 882 and 914 cm^{-1} for **1***, and at 700–850 (several overlapping Mo–O–Mo stretching vibrations), 904 and 940 cm^{-1} [ν(Mo = O)] for **2***. For **3*** and **4***, the spectra are consistent with the presence of the pyridinium β-octamolybdates $(C_5H_5NH)_4[Mo_8O_{26}]$ (**3***) and $((CH_3)_3CC_5H_4NH)_4[Mo_8O_{26}]$ (**4***), respectively. The former compound was previously obtained by the reaction of $MoO_3{\cdot}2H_2O$ with pyridine [61]. In accordance with that reported for pyridinium isopolymolybdates [61, 62], **3*** exhibits bands at 1633, 1609, 1532 and 1486 cm^{-1}, which indicate that the pyridine ring is protonated at the N atom. In the region of the Mo–O vibrations (500–950 cm^{-1}), the bands exhibited by **3*** (946, 912, 839, 802, 709, 675, 554 and 523 cm^{-1}) and **4*** (949, 914, 837, 799, 708, 659, 559 and 525 cm^{-1}) match those reported for other β-$[Mo_8O_{26}]^{4-}$ clusters [63, 64].



Scheme 1 Identified products in the reaction of MO with TBHP at 75 °C using complexes **1**–**4** as catalyst precursors

The reaction of MO with TBHP in the presence of **1***–**4*** (using the same molar ratios of Mo:MO:TBHP), at 75 °C, was much faster than that observed for the corresponding precursor complexes **1**–**4** (Fig. 1). These results may be partly due to the fact that the primary oxidative decarbonylation step is not required for the (pre-oxidized) complexes **1***–**4***, whereas it is necessary for **1**–**4**. The dependence of MES yield on MO conversion was similar for **1***–**4*** and at least 99 % MES yield could be reached within 24 h in all cases. A comparison of the MES selectivities at ca. 20–35 % conversion shows that the epoxide selectivity is poorer for the precursor complexes: 91 % (**1**), 93 % (**2**), 62 % (**3**), 71 % (**4**), >99 % (**1***–**4***). A likely explanation is that the in situ conversion of the precursor complexes is accompanied by oxidation of liberated iodide with TBHP to give molecular iodine and even (hypo)iodite ions, which may play a catalytic role favoring side reactions or epoxide ring opening [65, 66]. In parallel to that observed for the precursor complexes **1** and **2**, the reaction

Fig. 1 Kinetic profiles for the reaction of MO with TBHP, at 75 °C, in the presence of **1**–**4** (**a**) or **1***–**4*** (**c**), and the dependence of MES yield on MO conversion for **1**–**4** (**b**) or **1***–**4*** (**d**), using DCE as cosolvent: (*open diamond*)-**1**/**1***, (*open square*)-**2**/**2***, (*open triangle*)-**3**/**3***, (*open circle*)-**4**/**4***. Results for **1*** using the IL [bmim]BF_4 as cosolvent are also shown (*dashed lines* are visual guides): run 1 (*asterisk*), run 2 (*times*)



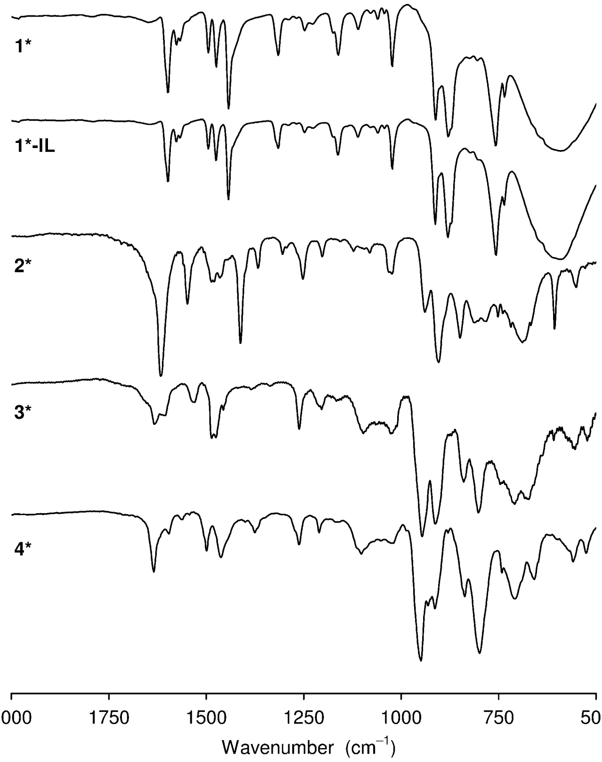


Fig. 2 FT-IR spectra of **1*** and **1***-IL (ATR), and **2***–**4*** (KBr disc)

of MO was faster for **2*** than for **1***. Some of us recently reported that the octanuclear complex $[Mo_8O_{22}(OH)_4(di\text{-}tBu\text{-}bipy)_4]$ is an active and selective catalyst in the reaction of MO with TBHP (39/82 % MES yield at 41/85 % conversion, reached at 6/24 h reaction, 1,2-dichloroethane as cosolvent, 55 °C) [54].

Compounds **3*** and **4*** are very active and gave similar results, which is consistent with the identification of both compounds as pyridinium *β*-octamolybdates. The presence of the *tert*-butyl substituent on the pyridinium counter-ion in **4*** does not significantly influence the reaction of MO: 97/99 % MES yield at 2/6 h reaction (Fig. 1). M. Jia and co-workers [67] recently reported that a *β*-octamolydate-based polyoxometalate modified by imidazole moieties and containing imidazolium counter-ions was an active catalyst for the epoxidation of olefins, and the catalytic reactions were heterogeneous in nature (e.g., 82 % conversion of *cis*-cyclooctene after 6 h reaction at 35 °C, initial molar ratio Mo:olefin:TBHP = 0.048:1:1, chloroform as solvent). Although compounds **3*** and **4*** did not dissolve completely in the reaction medium, the catalytic reactions took place at least to a certain extent in homogeneous phase. This was assessed in separate assays in which the solid phase was removed by filtration after 5 min reaction (at the reaction temperature of 75 °C), and the reaction taking place in the solution phase was monitored for a further 115 min. The increment in MO conversion in this time interval (Δfilt) was compared with that observed for the corresponding catalytic test without filtration (Δcat): values of Δfilt/Δcat were 0.3 for **3*** and 0.7 for **4*** (Δfilt/Δcat > 0 indicates the existence of a homogeneous catalytic contribution). The Δfilt/Δcat values may be less than unity due to the interruption of the dissolution of the metal species upon filtration of the solid at the initial stage of the reaction. For **1*** and **2***, Δfilt/Δcat = 1 (for **1***, filtration was performed at 1 h, further monitoring the reaction until 24 h; for **2***, filtration was performed at 5 min, further monitoring the reaction until 2 h), in agreement with the literature data [24].

ICP-OES of the liquid phases separated from the reaction mixtures after 6 h (MO conversion >82 %) by filtration through a 0.2 μm PTFE membrane filter indicated that the amount of dissolved molybdenum was 1, 30, 26 and 31 % of the initial molar amount of molybdenum for **1***, **2***, **3*** and **4***, respectively. Considering that for the four compounds the catalytic reaction is homogeneous in nature and assuming that all molybdenum centers of the dissolved compounds possess intrinsic catalytic activity, the turnover number at 6 h is highest for **1*** ($\mathrm{mol\ mol_{Mo}^{-1}}$): 8,180 (**1***) > 380 (**3***) ≅ 326 (**2***) ≅ 316 (**4***).

Since **1*** acts as a homogeneous catalyst the development of procedures for its separation from the reaction mixture and reuse is desirable. A possible approach consists of dissolving the catalyst in an IL, which poorly dissolves the substrate/products. The readily available and relatively cheap IL [bmim]BF_4 seems attractive and has been successfully employed in molybdenum-based catalytic systems for the epoxidation of a mixture of MO and methyl linoleate; [$MoO(O_2)_2$(8-quinolinol)$_2$], H_2O_2 and $NaHCO_3$ [52]. In the present work, the upper liquid phase consisted of MO which was hardly detected in the lower IL phase (ascertained by GC analysis). This IL-based catalytic system led to 86 % MES yield at 89 % conversion, 24 h, 75 °C (Fig. 1). After the first run, the reaction products were easily separated from the reaction mixture by adding *n*-hexane (immiscible with the IL; diethyl ether or ethyl acetate were similarly effective) to the reactor, followed by centrifugation and removal of the upper liquid phase. The complete removal of reactant/products from the IL mixture was checked by GC analysis. Prior to reuse, the IL mixture was treated at 40 °C under vacuum for 1 h. A second batch run was initiated by adding MO and TBHP to the IL mixture in the same amounts to those used in run 1. The kinetic behavior observed for run 2 is comparable to that of run 1, and the dependence of MES yield on MO conversion is roughly coincident for the two runs (Fig. 1). The ATR FT-IR spectrum of the recovered catalyst (washed with *n*-hexane and dried at room temperature overnight to give **1***-IL) was similar to that of **1*** (Fig. 2), suggesting that the catalyst is fairly stable and recyclable in the IL medium.

4 Conclusions

This work has shown that molybdenum(II) diiodo-tricarbonyl complexes containing either monodentate or bidentate nitrogen donor ligands are convenient precursors to oxomolybdenum(VI) catalysts for the selective epoxidation of MO using TBHP as oxidant. Reaction with the oxidant TBHP results in oxidative decarbonylation and loss of the iodo ligands, giving the one-dimensional molybdenum oxide/bipyridine polymer [MoO_3L] for L = 2,2′-bipyridine, octanuclear [$Mo_8O_{24}L_4$] for L = 4,4′-di-*tert*-butyl-2,2′-bipyridine, and the pyridinium *β*-octamolybdates $(LH)_4[Mo_8O_{26}]$ for L = pyridine or 4-*tert*-butylpyridine. Epoxide selectivity in the first run appears to be reduced due to the presence of oxidized iodine species in the reaction mixtures. This disadvantage is offset by the fact that the precursor complexes are easy to prepare from cheap starting materials, and in the second catalytic run using the recovered catalysts the epoxide selectivity was always at least 99 %. For the catalyst [MoO_3(bipy)], the use of an IL as cosolvent facilitates the separation of the reaction products. The IL phase including the Mo(VI) catalyst can be readily recycled by washing with hexane and drying, and the Mo(VI) catalyst can be reused without significant drop in catalytic performance.

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