ELSEVIER

Journal of Organometallic Chemistry 649 (2002) 108–112

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

New insights into the reaction of *t*-butylhydroperoxide with dichloro- and dimethyl(dioxo)molybdenum(VI)

Michelle Groarke [a], Isabel S. Gonçalves [a,b], Wolfgang A. Herrmann [a], Fritz E. Kühn [a,*]

[a] *Anorganisches-chemisches Institut der Technischen Universität München, Lichtenbergstraße 4, D-85747 Garching b, Munich, Germany*
[b] *Departamento de Química, Universidade de Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal*

Received 30 November 2001; accepted 2 December 2001

Abstract

Lewis-base adducts of dichlorodioxomolybdenum(VI) and dimethyldioxomolybdenum(VI) react in an equilibrium reaction with excess *t*-butylhydroperoxide (TBHP) under the formation of a seven-coordinated molybdenum(VI) complexes displaying a η^1-alkylperoxo-ligand. HCl/CH_4 elimination or the protonation of the Lewis-base ligand is not observed, the TBHP hydrogen atom is instead transferred to one of the terminal oxo ligands under the formation of a molybdenum bound –OH moiety. The peroxo species is assumed to be the active catalyst in olefin epoxidation.

Keywords: Alkylperoxides; Epoxidation; Molybdenum

1. Introduction

Lewis-base adducts of dihalogenodioxomolybdenum(VI) and dialkyldioxomolybdenum(VI) act as active catalysts in the olefin epoxidation when treated with high excess of *t*-butylhydroperoxide (TBHP) [1]. In the presence of hydrogen peroxide or triphenylmethyl-hydroperoxide they do not show catalytic activity, unless special Lewis bases are used [2]. While it is known that in the presence of H_2O_2 or Ph_3COOH η^2-mono- and bisperoxocomplexes of the types $MoClO(O_2)L$ and $MoO(O_2)_2L$ are formed [3], it is not clear to date, which kind of species could be formed in the presence of TBHP. In this work we present results, which give for the first time some closer insight into the reaction of TBHP with MoO_2X_2L. In order to be able to follow the reaction in solution we synthesized a soluble derivative MoO_2Cl_2L (**1**) and its alkyl homologue, $MoO_2(CH_3)_2L$ (**2**), with L = 4,4′-dihexyl-2,2′-bipyridine).

Table 1
Aromatic ^{1}H-NMR signals of 4,4′-bis(*n*-hexyl)bipyridine of selected compounds (in $CDCl_3$)

Compound **1**	9.39	8.06	7.49
1+TBHP	8.82	8.01	7.30
Compound **2**	9.38	8.04	7.51
2+TBHP	8.85	7.98	7.32
N-oxide	8.22	7.50	7.14
MoO_2Cl_2(*N*-oxide)	8.54	7.56	7.52
Protonated ligand	8.75	8.34	7.38
Free ligand	8.52	8.21	7.09

2. Results and discussion

First we examined whether the Mo(VI) complexes **1** and **2** exchange some of their ligands in solution. Excess of 4,4′-di-*tert*-butyl-2,2′-bipyridine was added to a solution of complex **1** and **2**, respectively, in CH_2Cl_2, the reaction mixtures were stirred for 4 h at 55° C and then ^{1}H-NMR and IR spectra were measured. No ligand exchange was observed. Reacting a solution of complex **1** with two equivalents of 2,2′-bipyridine, we also found that no significant ligand exchange was observed even after 2 days. The oxygens of the starting molybdenum complex are also found not to exchange with other terminal, metal bound oxygen ligands. This was confirmed by the treatment of a solution of compound **1** in $CDCl_3$ with ^{17}O labelled MTO, which is

* Corresponding author. Tel.: +49-89-289-13080; fax: +49-89-289-13473.
E-mail address: fritz.kuehn@ch.tum.de (F.E. Kühn).

0022-328X/02/$ - see front matter
PII: S0022-328X(02)01134-8

known to readily exchange its oxo functionality via intermolecular oxygen bridges [4]. After 2 days, NMR spectroscopy showed only the labelled rhenium oxygen signal.

It is also interesting to know whether the catalytically active species is formed in a reversible or irreversible manner with TBHP. Both complexes **1** and **2** were therefore reacted with a 300-fold excess of TBHP (5.5 M in *n*-decane solution, the same conditions as applied in our previous catalytic examinations) in CH_2Cl_2. When working up the reaction mixture we found that we obtained the starting complex unchanged in quantitative yield. This provides additional support for the conclusions drawn in a previous paper [1a] that the Mo–X bonds are not cleaved during the reaction with TBHP and indicates that the catalytically active species exists in an equilibrium with the starting complex in solution.

The reaction of compounds **1** and **2** with TBHP was then examined using spectroscopic tools. The bipyridine aromatic ^{1}H-NMR signals were used as diagnostic features in the elucidation of information. The addition of 0.5 equivalents of TBHP to complex **1** leads to new signals of very low intensity (see Table 1). Increasing the amount of TBHP leads to a slow increase in intensity of these new signals. During a period of more than 1 h new ^{1}H-NMR signals grow when a 1:6 excess of TBHP is applied, while the original signals lose integral intensity with respect to an internal standard. The development with higher amounts of TBHP is difficult to follow because of the large TBHP and solvent signals. However, applying a reaction temperature of 55° C leads to a faster reaction and a higher intensity of the product signals after a given time.120

We were initially concerned that the new signals were due to ligand oxidation. However, this was proven not to be the case (see Table 1). Moreover, it was found that adding alkylbipy-bis oxide ligands to MoO_2Cl_2 in a 1:1 fashion, leads to a different compound, the aromatic ^{1}H-NMR signals are also given in Table 1. We were also considering that the TBHP proton was transferred to the Lewis-base ligand. Thus, the free ligand was protonated with TFA, but the aromatic ^{1}H-NMR signals of the protonated species were found at different NMR shifts (Table 1). Therefore, protonation of the Lewis-base ligand may be excluded. It can also be assumed that protonation of the Lewis-base ligand would destabilize the complex resulting in its fast decomposition, a phenomenon, which was not observed to a significant extent. The overall up field shift of the aromatic ^{1}H signals from the free complex to the anomalous signals observed on treatment with TBHP could indicate a somewhat less Lewis acidic molybdenum core. This may be expected in case of coordination of the TBHP to the molybdenum. The results obtained for compound **2** were analogous to those obtained for compound **1** and seem to confirm the conclusions drawn above. Unfortunately, the CH_3-^{1}H-NMR signal was shifted to lower field (to ca. 0.9 ppm) in the case of the reaction of **2** with TBHP so that it could not be integrated due to heavy overlap with the *n*-hexyl groups of the Lewis-base ligands.

^{17}O-NMR experiments were also found to be quite informative on the reaction between compounds **1** and **2** with TBHP. ^{17}O labelled complex **1** exhibits a signal at 995 ppm with a linewidth of 800 Hz, compound **2** displays a signal at 845 ppm (linewidths 720 Hz). Upon addition of 0.5 equivalents of TBHP to compound **1**, a new small signal appears, at 563 ppm with a linewidth of 100 Hz (measurement time was ca. 15 min). In the case of compound **2** the new signal appears at 527 ppm (linewidths 140 Hz). The signal increases in size on addition of more TBHP and longer waiting times in both cases. The M=O signal does not change significantly on the incremental addition of TBHP and the linewidth remains constant. Unlabelled TBHP itself reveals two broad signals at 251 and 202 ppm with linewidths of 800 and 1050 Hz, respectively, which were not observed in the ^{17}O-NMR spectra. Molybdenum peroxo complexes exhibit their peroxo signals in a range of 400–600 ppm with linewidths of 1200–2000 Hz [5]. In our experiments, neither the chemical shift nor the linewidth was found to change for the signal at 563 and 527 ppm, respectively. Considering the fact that the TBHP oxygens are not evident in the NMR spectra, then it is highly unlikely that the peak at 563 (and 527, respectively) ppm is due to a minor amount of TBHP coordinated to the Mo centre. Therefore, we assume that this oxygen signal is due to a labelled oxygen of the complex. We propose that the proton of the TBHP is transferred to one of the terminal oxygens of the complex upon coordination of the TBHP to the molybdenum core. From literature precedent, the linewidth of ca. 100 Hz is obviously too narrow for a molybdenum peroxo species and a Mo–^{17}O–H is a reasonable assignment. Unfortunately, to the best of our knowledge, no ^{17}O signal of a similar complex has been reported in the literature to date.

^{95}Mo-NMR was explored as a tool to elucidate the electronic differences of the Mo core on reaction with TBHP. This involved sequential addition of TBHP solution in *n*-decane to a $CDCl_3$ solution of the complex. Up to a tenfold excess of TBHP was added. The molybdenum signal of complex **1** occurred at 192 ppm, displaying a half width of ca. 800 Hz (for complex **2** at 424 ppm, half width ca. 740 Hz). Addition of 0.5 equivalents of TBHP leads to a broadening of the signal in both cases but no significant shift change occurs. Adding more TBHP during ca. 1 h leads to further broadening (up to ca. 1500 Hz with three equivalents of TBHP). Until ten equivalents of TBHP are added, the signal is slowly shifted to 206 ppm in the

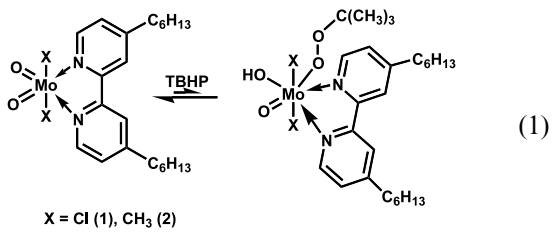
case of compound **1**, the linewidth remains very broad. A similar small downfield shift change is observed in the case of the methyl derivative ($\Delta\delta(^{95}\text{Mo}) = 16$ ppm for complex **2**). An explanation with respect to the results reported above may be that an equilibrium between the starting material and the reaction product with TBHP exists, which is located on the side of the starting materials. The mediated ^{95}Mo-NMR signal therefore strongly resembles that of the starting material, but is much broader.

Solution phase IR and Raman spectroscopies were used to examine the changes in stretching frequencies on reaction of complexes **1** and **2** with TBHP solutions in THF and CH_2Cl_2. The terminal Mo=O bonds of complex **1** show characteristic *cis* Mo=O stretching frequencies of 942 and 915 cm^{-1}. Small spectral changes are observed after addition of 0.5 equivalents of TBHP, which become very clear and pronounced after adding a tenfold excess of TBHP to the complex and an appropriate waiting time for establishing the equilibrium. A band at 978 cm^{-1} is observed, which increases in intensity on addition of TBHP to MoO_2Cl_2 (alkylbipy) solution. Additionally, two other bands at 885 and 593 cm^{-1} appear in both the IR and Raman spectra. The peaks attributable to the Mo=O stretching frequencies are found to decrease in intensity. The new bands can be reasonably assigned to the η^1-coordinated ^{t}BuOO$^-$ species and a protonated Mo=O. The new band at 980 cm^{-1} correlates to ν(M=O), the band at 885 cm^{-1} to ν(O–O) and the signal at 593 cm^{-1} to the ν(Mo–O). Mimoun et al. reports similar bands for the vanadium(V) η^1-peroxo complex, (dipic)VO(OO^{t}Bu) [dipic = 2,6-pyridinedicarboxylate] [6]. The latter complex exhibits a band at 980 cm^{-1} due to the terminal V=O, whereas the ν(O–O) stretching band occurs at 890 cm^{-1} and the ν(V–O) at 580 cm^{-1}. Molybdenum mono- and bis-η^2-peroxo species have also been reported in the literature [2,7]. The complex $MoO(O_2)Cl_2L$ (L = DMF, HPMT) shows the ν(O–O) band at 920 cm^{-1} whilst two bands at 550 and 600 cm^{-1} are found for the $Mo(O_2)$ stretching frequencies. $MoO(O_2)_2L_n$ (L = range of mono and bidentate N–O ligands) exhibit their peroxo ν(O–O) at 880 cm^{-1} and the ν(Mo–O) is highlighted by two bands at 500 and 600 cm^{-1}. Analogous bands are not found in our experiments, therefore, we can confidently exclude the possibility of the formation of a η^2-mono- or bisperoxo species. A shoulder at approximately 3270 cm^{-1} appears in the IR spectra on addition of one equivalent of TBHP, which broadens (3300 cm^{-1}) after the addition of excess TBHP to the complex solution. This is suggestive of a different OH species to the TBHP–OH. We were concerned that this might merely be due to moisture in the sample. However, the presence of moisture would be confirmed by a band at ca. 1600 cm^{-1}. This band was conspicuously absent. Thus, it is reasonable to assume that the 3300 cm^{-1} band can be ascribed to a Mo–OH vibration. The results obtained for derivative **2** were analogous. Additionally, the Mo–C IR-vibrations at 495 cm^{-1} (asymmetric vibrations) and 470 cm^{-1} (symmetric vibrations) remained observable during all our experiments and were shifted less than 20 cm^{-1} (to 479 and 457 cm^{-1}, respectively), so the cleavage of these particular bonds seems not to be of major concern under the conditions applied. The Mo–C interaction, however, seems to weaken. The intensity loss of the bands might also be attributed to the changes in the structure of the complex due to the reaction with TBHP.

We were also interested in gaining information on the mode of coordination of the TBHP to the molybdenum centre, i.e. whether initial protonation of a Mo=O occurs followed by coordination of the ^{t}BuOO$^-$ or coordination of the TBHP to the Mo is the first step followed by proton transfer to the M=O. We examined the reaction between complex **1** and TFA and it was found that no changes occurred in the ^{1}H-NMR spectrum even after 2 days. Complex decomposition was not observed. This suggests that the Mo=O is not sufficiently basic to be protonated even by such a strong acid. It is also argued that the triflate anion has an insufficient coordinating ability due to the electron withdrawing capacity of the CF_3 group. This strongly suggests that coordination of the TBHP is a prerequisite for proton transfer. Considering the pK_a of TBHP (ca. 11), it was decided to compare its coordination with an alcohol of similar pK_a. Phenol was chosen, having a pK_a of 10. It was found that the phenol ^{1}H-NMR signals remained unchanged on reaction with complex **1** and the phenolic O–H was still evident. It might be that the phenol is too sterically demanding to coordinate to the molybdenum core and, as proton transfer is not observed, then it may be assumed that coordination of the alcohol is required before the Mo=O may be protonated. It can, in principle, not be totally excluded that instead of an ionic transfer mechanism a radicalic transfer of the proton from TBHP takes place. To elucidate if the mechanism involves radical pathways an experiment was carried out with complexes **1** and **2** in the presence of a radical scavenger added at the beginning of the reaction (equimolar amounts of cyclooctene and 2,6-di-*tert*-butyl-4-methylphenol). The reaction rate was not significantly affected, therefore not supporting the involvement of radical species, which are not extremely short lived.

In summary, based on the experimental data presented above, it seems reasonable to assume that the reaction of Lewis-base adducts of dichloro- and dimethyl(dioxo)molybdenum(VI) with excess TBHP produce products of the composition shown in Eq. (1). Additional kinetic and theoretic examinations are cur-

rently under way in our laboratory and will be published elsewhere.



(1)

3. Experimental

All preparations and manipulations were done with standard Schlenk techniques under an atmosphere of nitrogen. Solvents were dried by standard procedures, distilled under Ar and kept over 4 Å molecular sieves (3 Å for NCMe). Microanalyses were performed at the Mikroanalytische Labor of the Technische Universität München in Garching (M. Barth). ^{1}H-NMR spectra were recorded at 400 MHz in a Bruker Avance DPX-400 spectrometers. ^{17}O-NMR spectra were measured at 54.14 MHz in a Bruker Avance DPX-400, and ^{95}Mo-NMR spectra were measured at 26.07 MHz. Infrared spectra of solid samples (in the form of KBr pellets and Nujol mulls) were measured in a Bio-Rad FTS-60A. The far infrared spectra of the complexes were recorded as Nujol mulls in a Bio-Rad FTS-175A system using a 6 mm Mylar beam splitter. The Raman spectra were also performed with a Bio-Rad dedicated FT-Raman spectrometer using the 1064 nm excitation of an Nd-YAG laser.

3.1. Preparation of 4,4′-bishexyl-2,2′-bipyridine

n-BuLi in hexane (17.5 ml, 28 mmol, 1.6 M) was added dropwise to a solution of diisopropyl amine (3.9 ml, 28 mmol) in THF (10 ml) at 0° C. 4,4′-Dimethyl-2,2′-bipyridine (2 g, 11 mmol) dissolved in THF (50 ml) was added slowly to the reaction mixture and the resulting red solution was stirred at 0° C for 3 h. A solution of amyl bromide (3.5 ml, 28 mmol) was then added and the reaction mixture was stirred overnight, reaching slowly the room temperature (r.t.). The reaction was quenched by the addition of MeOH and the solution was poured onto ice. The crude product was extracted with Et_2O and purified by chromatography on silica using EtOAc–*n*-hexane (40–60) as eluent to yield the pure product as a pale yellow oil, 2.5 g (70%). Calc. for $C_{22}H_{32}N_2$ (324.51 g mol^{-1}): C, 81.43; H, 9.94; N, 8.63. Found: C, 81.12; H, 9.84; N, 9.04%. ^{1}H-NMR (400 MHz, $CDCl_3$), 0.84 (6H, m, CH_3), 1.19 (4H, m, CH_2), 1.27 (8H, m, $(CH_2)_2$), 1.65 (4H, m, CH_2), 2.64 (4H, m, CH_2), 7.09 (2H, m, py–H), 8.21 (2H, m, py–H), 8.52 (2H, m, py–H).

3.2. Preparation of MoO_2Cl_2(n-hexylbipy) (1)

4,4′-Dihexyl-2,2′-bipyridine (0.84 g, 2.60 mmol) was added to a suspension of MoO_2Cl_2 (0.47 g, 2.36 mmol) in CH_2Cl_2 (5 ml) and the resulting solution was stirred for 30 min. The solution was filtered and concentrated to 1 ml and hexane was added to precipitate the colourless product, which was purified by washing with hexane. The colourless solid was collected and dried in vacuo to yield the title complex, 1.19g (96%). Calc. for $C_{22}H_{34}Cl_2MoN_2O_2$ (525.36 g mol^{-1}): C, 50.49; H, 6.16; N, 5.35. Found: C, 50.80; H, 6.40; N, 5.16%. Selected IR data: (KBr, ν cm^{-1}): 3071 w, 2939 s, 1610 s, 937 vs, 912 vs, 895 m, 623 w, 344 m, 237 m; ^{1}H-NMR (400 MHz, $CDCl_3$); 0.92 (6H, t, CH_3), 1.36 (8H, m, $(CH_2)_2$), 1.43 (4H, m, CH_2), 1.76 (4H, m, CH_2), 2.84 (4H, t, CH_2), 7.50 (2H, d, py–H), 8.06 (2H, s, py–H), 9.39 (2H, d, py–H).

3.3. Preparation of $MoO_2(CH_3)_2$(n-hexylbipy) (2)

To a suspension of 0.53 g (1.0 mmol) **1** in Et_2O at −25° C (isopropanol bath), 2.1 equivalents of a 1.0 molar solution MeMgCl dissolved in Et_2O was slowly added via syringe. The reaction was allowed to warm-up to r.t. and was stirred for 90 min. The dark red suspension was dried and distilled water was added. The product was extracted with CH_2Cl_2 and the organic phase was dried over anhydrous $MgSO_4$. The solvent was dried and the yellow residue was recrystallised from CH_2Cl_2–Et_2O. Yield: 0.25 g (52%). Calc. for $C_{22}H_{38}MoN_2O_2$ (482.26 g mol^{-1}): C, 59.74; H, 7.94; N, 6.81. Found: C, 60.06; H, 7.99; N, 6.74%. IR (KBr, ν cm^{-1}): 3055 m, 2953 vs, 2907 s, 2871 s, 1611 s, 930 vs, 906, vs, ν(Mo=O), 880 m, 618 s. 495 m, 470 w. ^{1}H-NMR (400 MHz, $CDCl_3$); 0.59 (s, 6H), 0.90 (6H, t, CH_3), 1.35 (8H, m, $(CH_2)_2$), 1.40 (4H, m, CH_2), 1.72 (4H, m, CH_2), 2.79 (4H, t, CH_2), 7.51 (2H, d, py–H), 8.04 (2H, s, py–H), 9.38 (2H, d, py–H).

3.4. ^{17}O-labelling studies

The labelled complex $Mo^{17}O_2Cl_2(DMF)_2$ was prepared according to the published procedure using $H_2^{17}O$ [8] [1b]. Labelled complex $Mo^{17}O_2Cl_2(THF)_2$ was prepared by recrystallisation of $Mo^{17}O_2Cl_2(DMF)_2$ from THF. Labelled complex $Mo^{17}O_2X_2L$ (X = Cl, Me) was prepared using the usual method with the labelled starting material $Mo^{17}O_2Cl_2(NCMe)_2$.

Acknowledgements

I.S.G. acknowledges the Bayerische Forschungsstiftung for a research grant. M.G. thank the Alexander von Humboldt-foundation for a postdoctoral research

fellowship. Dr P. Ferreira, Dr A.M. Santos and Dr É. Bencze are acknowledged for helpful assistance.

References

[1] (a) F.E. Kühn, A.M. Santos, I.S. Gonçalves, C.C. Romão, A.D. Lopes, Appl. Organomet. Chem. 15 (2001) 43 (and references therein);
(b) F.E. Kühn, A.M. Santos, A.D. Lopes, I.S. Gonçalves, J.E. Rodríguez-Borges, M. Pillinger, C.C. Romão, J. Organomet. Chem. 621 (2001) 207;
(c) A.M. Santos, F.E. Kühn, K. Bruus-Jensen, I. Lucas, C.C. Romão, E. Herdtweck, J. Chem. Soc. Dalton Trans. (2001) 1332;
(d) I.S. Gonçalves, C.C. Romão, A.M. Santos, A.D. Lopes, J.E. Rodrígues-Borges, M. Pillinger, P. Ferreira, F.E. Kühn, J. Rocha, J. Organomet. Chem. 626 (2001) 1;
(e) A.A. Valente, I.S. Gonçalves, A.D. Lopes, J.E. Rodríguez-Borges, M. Pillinger, C.C. Romão, J. Rocha, X. García-Mera, New J. Chem. 25 (2001) 959.

[2] (a) G. Wahl, D. Kleinhenz, A. Schorm, J. Sundermeyer, R. Stohwasser, C. Rummey, G. Bringmann, C. Fickert, W. Kiefer, Chem. Eur. J. 5 (1999) 3237;
(b) A. Hroch, W.R. Thiel, Eur. J. Inorg. Chem. 3 (2000) 1107 (and references therein).

[3] P. Chaumette, H. Mimoun, L. Saussine, J. Fischer, A. Mitschler, J. Organomet. Chem. 250 (1983) 291.

[4] (a) P. Gisdakis, N. Rösch, É. Bencze, J. Mink, I.S. Gonçalves, F.E. Kühn, Eur. J. Inorg. Chem. (2001) 981;
(b) W.A. Herrmann, F.E. Kühn, M.U. Rauch, J.D.G. Correia, G. Artus, Inorg. Chem. 34 (1995) 2914.

[5] M.S. Reynolds, A. Butler, Inorg. Chem. 35 (1996) 2378 (and references therein).

[6] H. Mimoun, P. Chaumette, M. Mignard, L. Saussine, J. Fischer, R. Weiss, Nouv. J. Chim. 7 (1983) 467.

[7] W.P. Griffith, T.D. Wickins, J. Chem. Soc. Sect. A (1968) 397.

[8] (a) P. Chaumette, H. Mimoun, L. Saussine, J. Fischer, A. Mitschler, J. Organomet. Chem. 250 (1983) 291;
(b) E.P. Talsi, O.V. Klimov, K.I. Zamaraev, J. Mol. Catal. 83 (1993) 329;
(c) E.P. Talsi, K.V. Shalyaev, K.I. Zamaraev, J. Mol. Catal. 83 (1993) 347.