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Synthesis, characterization and catalytic activity of addition compounds of dioxomolybdenum(VI) pyridine-2,6-dicarboxylate. Crystal structure of MoO_2(dipic)(L) (L = DMF, DMSO, $OPPh_3$)

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Abstract

MoO_2(dipic)(L) (dipic = pyridine 2,6-dicarboxylate (dipicolinate); L = dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), hexamethyl phosphorotriamide (HMPA), triphenylphosphine oxide ($OPPh_3$), triethylamine, tripropylamine, tributylamine, pyridine, 2-methylpyridine, 3-methylpyridine, 4-methylpyridine) have been prepared by reacting equimolar amounts of $MoO_2Cl_2(L)_2$ (L = DMF, DMSO) with Na_2dipic, followed by addition of the appropriate ligand to the resulting solutions. The molecular structures of the DMF, DMSO and HMPA derivatives have been established by X-ray diffraction analysis. The ability of MoO_2(dipic)(L) (L = DMF, DMSO, HMPA, $OPPh_3$) to work as oxotransfer catalysts has been examined and compared with that of the prototypical $MoO_2(Et_2dtc)_2$ (Et_2dtc = diethyl dithiocarbamate). Dipicolinate complexes proved to be more efficient catalysts than dithiocarbamate for the deoxygenation of azoxybenzene with triphenylphosphine in boiling toluene.

Keywords: Dioxomolybdenum dipicolinate; Oxygen-atom transfer; Azoxybenzene deoxygenation

1. Introduction

It has been assumed for years that the presence of sulfur atoms coordinated to molybdenum is a requisite for complexes of this metal to have oxotransfer activity, and many model compounds that mimic oxotransferases have been studied [1–7]. The first oxotransfer reaction involving a molybdenum complex without coordinated sulfur atoms was reported in 1990 [8]. This observation proved that the presence of sulfur atoms coordinated to molybdenum is not essential for oxotransfer activity in mild conditions, and since then a number of complexes of this kind have been reported [9–14]. One of the most relevant is the anionic $[MoO_2(NCS)_4]^{2-}$ species, which contains *N*-coordinated thiocyanate and has a catalytic activity greater than that of the prototypical $MoO_2(Et_2dtc)_2$ in the oxidation of PPh_3 with DMSO [9]. More recently the catalytic activity of $MoO_2(CH_3)_2(L)$ (L = bipyridine, alkyl substituted bipyridine) [15], and that of MoO_2[2,6-bis(mentyl)pyridine)] in oxotransfer processes has been mentioned [16]. In our laboratory we found that simple, air-stable complexes derived from MoO_2Cl_2 and MoO_2Br_2 are also superior to dithiocarbamates in the oxygen atom transfer from DMSO to PPh_3 at room temperature [13,14,17]. This prompted us to search for new dioxomolybdenum(VI) compounds in order to test their potentiality as oxotransfer catalysts. Here we report on the synthesis, characterization and catalytic activity of a number of dipicolinate complexes.

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2. Experimental

2.1. General procedures and measurements

All operations were carried out in a dry oxygen-free nitrogen atmosphere using standard Schlenck techniques, except the synthesis of the compounds with DMF, DMSO, HMPA and $OPPh_3$ which were conducted in air. Diethyl ether and toluene were distilled from sodium under nitrogen prior to use. *N*,*N*-Dimethylformamide was dried with barium oxide and distilled under reduced pressure. Acetone and amines for the preparation of amine complexes were distilled immediately before use. Triphenylphosphine was recrystallized prior to use and checked by ^{31}P NMR and melting point for purity. All other reagents were commercial products and were used without further purification. $MoO_2Cl_2(DMSO)_2$ and $MoO_2Cl_2(DMF)_2$ were prepared as reported [13]. Na_2dipic was prepared by reacting equimolar amounts of Na_2CO_3 and H_2dipic in water, crystallizing the resulting solution and heating the solid at 100°C under vacuum for 5 h. Melting points were determined with a Buchi 'Tottoli' with variable warm speed. Elemental analyses (C, H, N) were performed on a Perkin–Elmer 2400 CHN analyzer and molybdenum was determined by titration with lead(II) nitrate [18]. IR spectra were recorded on a Perkin–Elmer 843 spectrometer with Heyden and Son Spectrafile-IR version 2.2 operating software, and UV–Vis spectra on a Milton Roy Spectronic 3000 Arrays spectrometer equipped with a thermostated cell. NMR spectra were recorded on a Bruker AC-300 and a Bruker DPX 300 spectrometer (^1H, 300 MHz; ^{31}P, 121.5 MHz). Chemical shifts are relative to TMS (^1H), or external 85% H_3PO_4 (^{31}P), with downfield values reported as positive. Coupling constants J are given in Hz.

2.2. General procedure for the preparation of MoO_2(dipic)(L) (L = DMF, DMSO, HMPA, $OPPh_3$)

A mixture of Na_2dipic (2.11 g, 10.5 mmol), $MoO_2Cl_2(DMF)_2$ (3.45 g, 10 mmol) and L (12 mmol) in acetone (60 ml) was refluxed with stirring for 1 h. The white precipitate was separated by filtration and washed with acetone (10 ml). The combined filtrate and washing was concentrated to 10 ml and then diethyl ether (50 ml) was added. The resulting light yellow microcrystalline precipitate was filtered, washed with diethyl ether (2 × 10 ml) and dried under vacuum.

2.2.1. MoO_2(dipic)(DMF)

Yield 3.07 g (83.8%). — M.p. (dec.) 200–202°C. — IR (KBr) cm^{-1}: $\nu(MoO_2) = 942$ s, 905 s; $\nu(CO_2) = 1693$ s, 1489 s; ν(C=O, DMF) = 1637 s. — ^1H NMR (300 MHz, acetone-d_6, 25°C, TMS): $\delta = 8.85$ (t, $J = 7.63$, 1H, dipic), 8.46 (d, $J = 7.63$, 2H, dipic), 8.19 (s, 1H, H–CO), 3.06 (s, 3H, CH_3), 2.62 (s, 3H, CH_3). — *Anal.* Calc. for $C_{10}H_{10}MoN_2O_7$ (367.96): Mo 26.20, C 32.81, H 2.75, N 7.65. Found: Mo 26.12, C 31.67, H 2.87, N 7.56%.

2.2.2. MoO_2(dipic)(DMSO)

Yield 3.40 g (91.6%). — M.p. (dec.) 185–187°C. — IR (KBr) cm^{-1}: $\nu(MoO_2) = 942$ s, 909 s; $\nu(CO_2) = 1707$ s, 1470 s; ν(S=O) = 1081 s. — ^1H NMR (300 MHz, acetone-d_6, 25°C, TMS): $\delta = 8.81$ (t, $J = 7.73$, 1H, dipic), 8.45 (d, $J = 7.73$, 2H, dipic), 2.69 (s, 6H, CH_3). — *Anal.* Calc. for $C_9H_9MoNO_7S$ (372.92): Mo 25.85, C 29.12, H 2.44, N 3.77. Found: Mo 25.73, C 29.24, H 2.39, N 3.79%.

2.2.3. MoO_2(dipic)(HMPA)

Yield 3.62 g (76.7%). — M.p. (dec.) 234–236°C. — IR (KBr) cm^{-1}: $\nu(MoO_2) = 934$ s, 912 s; $\nu(CO_2) = 1707$ s, 1466 s; ν(P=O) = 1192 s; ν(HMPA) = 1303, 993 and 756. — ^1H NMR (300 MHz, acetone-d_6, 25°C, TMS): $\delta = 8.76$ (t, $J = 7.76$, 1H, dipic), 8.43 (d, $J = 7.76$, 2H, dipic), 2.46 (d, $J_{HP} = 9.63$, 18H, CH_3). — ^{31}P NMR (121.5 MHz, acetone-d_6, 25°C, H_3PO_4): $\delta = 29.60$. — *Anal.* Calc. for $C_{13}H_{21}MoN_4O_7P$ (474.02): Mo 20.32, C 33.06, H 4.48, N 11.86. Found: Mo 20.22, C 32.18, H 4.30, N 11.68%.

2.2.4. MoO_2(dipic)($OPPh_3$)

Yield 4.20 g (73.5%). — IR (KBr) cm^{-1}: $\nu(MoO_2) = 940$ s, 910 s; $\nu(CO_2) = 1710$ s, 1585 s; ν(P=O) = 1154 s. — ^1H NMR (300 MHz, acetone-d_6, 25°C, TMS): $\delta = 8.71$ (t, $J = 7.76$, 1H, dipic), 8.31 (d, $J = 7.93$, 2H, dipic), 7.7–7.5 (m, 15H, C_6H_5). — ^{31}P NMR (121.5 MHz, acetone-d_6, 25°C, H_3PO_4): δ = 33.07. — *Anal.* Calc. for $C_{25}H_{18}MoNO_7P$ (572.99): Mo 16.79, C 52.56, H 3.27, N 2.45. Found: Mo 16.62, C 52.42, H 3.23, N 2.50%.

2.3. General procedure for the preparation of MoO_2(dipic)(amine) (amine = pyridine (Py), 2-methylpyridine (2-MePy), 3-methylpyridine (3-MePy), 4-methylpyridine (4-MePy), triethylamine (NEt_3), tripropylamine (NPr_3), tributylamine (NBu_3))

To a solution of MoO_2(dipic)(DMF) (1.46 g, 4 mmol) in acetone (20 ml) a solution of amine (4.2 mmol) in acetone (5 ml) is added. After stirring the resulting mixture for 5 min, the white precipitate is filtered, washed with acetone (2 × 5 ml) and diethyl ether (2 × 10 ml), and dried under vacuum.

2.3.1. MoO_2(dipic)(Py)

Yield 1.41 g (95%). — IR (KBr) cm^{-1}: $\nu(MoO_2) =$ 946 s, 919 s; $\nu(CO_2) = 1730$ s, 1484 s. — *Anal.* Calc. for $C_{12}H_8MoN_2O_6$ (372.14): Mo 25.78, C 38.73, H 2.17, N 7.53. Found: Mo 25.35, C 38.52, H 2.32, N 7.25%.

2.3.2. MoO_2(dipic)(2-MePy)

Yield 1.03 g, (67%). — IR(KBr) cm^{-1}: $\nu(MoO_2)$ = 946 s and 918 s; $\nu(CO_2)$ = 1726 s, 1431 s. — *Anal.* Calc. for $C_{13}H_{10}MoN_2O_6$ (386.17): Mo 24.85, C 40.43, H 2.61, N 7.25. Found: Mo 24.85, C 40.13, H 2.38, N 7.07%.

2.3.3. MoO_2(dipic)(3-MePy)

Yield 1.24 g, (80%). — IR(KBr) cm^{-1}: $\nu(MoO_2)$ = 947 s, 914 s; $\nu(CO_2)$ = 1726 s, 1455 s. — *Anal.* Calc. for $C_{13}H_{10}MoN_2O_6$ (386.17): Mo 24.85, C 40.43, H 2.61, N 7.25. Found: Mo 23.96, C 39.62, H 2.57, N 6.95%.

2.3.4. MoO_2(dipic)(4-MePy)

Yield 1.32 g, (85%). — IR(KBr) cm^{-1}: $\nu(MoO_2)$ = 942 s, 908 s; $\nu(CO_2)$ = 1730 s, 1433 s. — *Anal.* Calc. for $C_{13}H_{10}MoN_2O_6$ (386.17): Mo 24.85, C 40.43, H 2.61, N 7.25. Found: Mo 24.98, C 39.86, H 2.77, N 6.96%.

2.3.5. MoO_2(dipic)(NEt_3)

Yield 1.17 g, (74%). — IR(KBr) cm^{-1}: $\nu(MoO_2)$ = 942 s, 912 s; $\nu(CO_2)$ = 1609 s, 1447s. — *Anal.* Calc. for $C_{13}H_{18}MoN_2O_6$ (394.24): Mo 24.34, C 39.61, H 4.60, N 7.11. Found: Mo 24.03, C 39.35, H 4.72, N 7.25%.

2.3.6. MoO_2(dipic)(NPr_3)

Yield 1.08 g, (62%). — IR(KBr) cm^{-1}: $\nu(MoO_2)$ = 937 s, 909 s; $\nu(CO_2)$ = 1690 s, 1470 s. — *Anal.* Calc. for $C_{16}H_{24}MoN_2O_6$ (436.32): Mo 21.99, C 44.04, H 5.54, N 6.42. Found: Mo 22.54, C 45.04, H 5.70, N 6.22%.

2.3.7. MoO_2(dipic)(NBu_3)

Yield 1.72 g, (90%). — IR(KBr) cm^{-1}: $\nu(MoO_2)$ = 939 s, 910 s; $\nu(CO_2)$ = 1684 s, 1467 s. — *Anal.* Calc. for $C_{19}H_{30}MoN_2O_6$ (478.40): Mo 20.26, C 47.70, H 6.32, N 5.86. Found: Mo 19.50, C 46.96, H 6.10, N 5.68%.

2.4. Preparation of Mo_2O_3(dipic)$_2$($OPPh_3$)$_2$

2.4.1. Method A

A mixture of MoO_2(dipic)($OPPh_3$) (0.71 g, 1.25 mmol) and PPh_3 (0.33 g, 1.25 mmol) in toluene (30 ml) was refluxed for 1 h under nitrogen. The dark brown powdered precipitate is filtered, washed with diethyl ether and dried under vacuum (0.61 g, 87%).

2.4.2. Method B

A mixture of MoO_2(dipic)($OPPh_3$) (0.71 g, 1.25 mmol) and PPh_3 (0.33 g, 1.25 mmol) in acetone (30 ml) was refluxed for 2 h under nitrogen. The resulting solution is concentrated to 10 ml and then treated with diethyl ether (30 ml). The dark brown precipitate is filtered, washed with diethyl ether and dried under vacuum (0.63 g, 89.5%).

IR(KBr) cm^{-1}: $\nu(MoO_2)$ = 953 s, 914 s; $\nu(CO_2)$ = 1688 s, 1438 s; $\nu(P{=}O)$ = 1160 s. — ^1H NMR (80 MHz, $CDCl_3$, 25°C, TMS): δ = 8.0–8.4 (m, J = 7.76 Hz, 3H, dipic), 7.4–7.6 (m, 15H, C_6H_5). — *Anal.* Calc. for $C_{50}H_{36}Mo_2N_2O_{13}P_2$ (1129.99): Mo 17.03, C 53.30, H 3.22, N 2.49. Found: Mo 17.23, C 53.12, H 3.06, N 2.32%.

2.5. Catalytic activity

The measurement of the catalytic activity of MoO_2(dipic)(DMSO) in the oxidation of triphenyl phosphine with dimethyl sulfoxide was followed by ^{31}P NMR spectroscopy, and compared with that of $MoO_2(Et_2dtc)_2$, as previously reported [13]. Two 5 ml DMSO (20% v/v in DMSO-d_6) solutions, at [Mo] = 0.02 mol dm^{-3} and [PPh_3] = 0.40 mol dm^{-3}, were used. At 25°C the oxidation of 50% PPh_3 required 175 min in the dipicolinate solution and 85 min in that of the dithiocarbamate. PPh_3 became undetectable with the former after 7 h. Solid PPh_3 (50 mg) was added to the dipicolinate solution that was examined after 4 h showing only the presence of $OPPh_3$. The same result was obtained when this operation was repeated after 2, 4 and 7 days.

2.6. Deoxygenation of azoxybenzene

The deoxygenation of azoxybenzene was followed in toluene at 105°C monitoring the reaction by visible spectroscopy. Samples of 2 ml were collected off by syringe from the reacting system at regular intervals, and immediately transferred to graduated rubber-capped tubes, containing 2 ml of 4 M NaOH, immersed into an ice bath. After vigorous shaking of the tubes to remove the molybdenum complexes from the toluene phase the absorbance was measured at 446 nm, wavelength at which azobenzene is the only absorbing species present in toluene.

2.7. Crystal-structure determinations

Suitable single crystals were grown at room temperature by diffusion of diethyl ether on acetone solutions of the complexes in a dry atmosphere. Crystal data MoO_2(dipic)(DMF) were collected using an Enraf–Nonius MACH3 diffractometer with graphite-monochromated Mo Kα radiation. Crystal data for the complexes MoO_2(dipic)(DMSO) and MoO_2(dipic)($OPPh_3$) were collected using a KappaCCD diffractometer with graphite-monochromated Mo Kα radiation. Hydrogen atom positions were located from difference Fourier maps. All three structures were solved using OPENMOLEN

2.2. Table 1 provides crystallographic details for these compounds.

3. Results and discussion

3.1. Synthesis and characterization of the complexes

To the best of our knowledge only a marginal reference to the synthesis and characterization by melting point and infrared spectroscopy of MoO_2(dipic)-(HMPA) has been reported [19]. More recently, in studies on the reactivity of molybdenaoxaziridine complexes, the formation of Mo_2O_3(dipic)$_2$(HMPA)$_2$ was postulated [20]. MoO_2(dipic)(HMPA) was prepared by reacting MoO_2(acac)$_2$ (acac = acetylacetonate) with dipicolinic acid and HMPA in CH_2Cl_2. In these conditions a green solution was obtained which suggests that a redox process also occurs, probably involving the acacH displaced.

To overcome this difficulty we have used the easily available $MoO_2Cl_2(L)_2$ (L = DMF, DMSO) [17] complexes instead of MoO_2(acac)$_2$. Metathetic reactions between the disodium salt of dipicolinic acid and the corresponding chlorocomplex in acetone proved to be appropriate for preparing MoO_2(dipic)(DMF) and MoO_2(dipic)(DMSO). The reaction requires about 24 h at room temperature for completion, probably because Na_2dipic is scarcely soluble in acetone, but less than 1 h when carried out to reflux. The compounds are recovered in good yield from the resulting solutions by removing most of the solvent under vacuum followed by precipitation with diethyl ether.

MoO_2(dipic)(L) (L = HMPA, $OPPh_3$, tertiary amine) were prepared by treating acetone solutions of MoO_2(dipic)(DMF) or MoO_2(dipic)(DMSO) with the corresponding ligand. MoO_2(dipic)(HMPA) and MoO_2(dipic)($OPPh_3$) are obtained by addition of diethyl ether to the resulting solutions, while the amine derivatives separated as fine white precipitates; further studies for the complete characterization of the latter are in progress. MoO_2(dipic)(HMPA) and MoO_2-(dipic)($OPPh_3$) can also be prepared by reacting $MoO_2Cl_2(L)_2$ (L = DMF, DMSO) with Na_2dipic in presence of the corresponding ligand, followed by filtration of NaCl and addition of diethyl ether to the resulting solution. In this regard the DMF complex is superior to that of DMSO since DMF is miscible with diethyl ether. The presence of minor amounts of water either in Na_2dipic or in the solvent has not significant effect on the preparation of the derivatives with DMF, DMSO, HMPA and $OPPh_3$ since these ligands are able to displace water from the coordination sphere of molybdenum. Also they have a low affinity for protons, thus precluding the formation of polymolybdates. By the contrary, the high proton basicity of tertiary amines requires the use of rigorously anhydrous conditions to obtain pure products.

No relevant features are observed in the IR spectra of the compounds. The presence of two bands in the region 900–950 cm^{-1} indicates that, as usual for dioxomolybdenum(VI) species, all the complexes contain

Table 1
Crystal data and summary of intensity data collection and structure refinement of complexes MoO_2(dipic)(DMF), MoO_2(dipic)(DMSO) and MoO_2(dipic)($OPPh_3$)

	MoO_2(dipic)(DMF)	MoO_2(dipic)(DMSO)	MoO_2(dipic)($OPPh_3$)
Empirical formula	$C_{10}H_{10}MoN_2O_7$	$C_9H_9MoNO_7S$	$C_{25}H_{18}MoNO_7P$
Molecular weight	366.14	371.18	571.34
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P12_1/n1$
Unit cell dimensions			
a (Å)	7.1627(9)	6.627(1)	9.5225(3)
b (Å)	7.991(1)	7.619(1)	17.9542(6)
c (Å)	13.486(4)	12.793(1)	14.5104(4)
α (°)	72.21(2)	97.164(4)	
β (°)	79.49(2)	101.912(4)	107.537(2)
γ (°)	62.19(1)	93.063(4)	
V (Å^3)	649.4(2)	625.0(2)	2365.5(2)
Z	2	2	4
D_{calc} (g cm^{-3})	1.87	1.97	1.60
μ (mm^{-1})	1.043	1.244	0.669
Number of data measured	2737	8656	18322
Number of data with $I>3\sigma(I)$	2320	2586	5009
Scan mode	$\theta/2\theta$	ϕ and ω scans	phi scans
T (K)	294	294	173
R	0.025	0.027	0.040
wR	0.041	0.043	0.056
Goodness-of-fit (GOF)	1.012	1.094	1.043

Table 2
Selected bond lengths (Å) and angles (°) for MoO_2(dipic)(DMF), MoO_2(dipic)(DMSO) and MoO_2(dipic)($OPPh_3$)

	MoO_2(dipic)(DMF)	MoO_2(dipic)(DMSO)	MoO_2(dipic)($OPPh_3$)
Mo(1)–O(5)	1.674(2)	1.696(2)	1.687(2)
Mo(1)–O(6)	1.702(2)	1.703(2)	1.700(2)
Mo(1)–O(1)	2.009(2)	2.008(2)	2.003(2)
Mo(1)–O(4)	2.010(2)	2.017(2)	2.000(2)
Mo(1)–N(1)	2.190(2)	2.198(2)	2.205(2)
Mo(1)–O(7)	2.308(2)	2.312(2)	2.247(2)
O(4)–C(7)	1.320(4)	1.335(3)	1.326(3)
O(1)–C(1)	1.325(4)	1.334(3)	1.325(3)
O(7)–X	1.233(4)	1.544(2)	1.502(2)
O(5)–Mo(1)–O(6)	105.5(1)	104.7(1)	104.6(1)
O(1)–Mo(1)–O(4)	144.68(9)	144.81(7)	145.43(8)
O(6)–Mo(1)–O(4)	106.5(1)	101.82(8)	103.86(9)
O(6)–Mo(1)–O(1)	101.8(1)	106.90(9)	104.73(8)
N(1)–Mo(1)–O(4)	72.48(8)	72.56(7)	72.95(8)
N(1)–Mo(1)–O(1)	72.79(8)	73.12(7)	73.03(7)
O(5)–Mo(1)–O(4)	95.8(1)	94.49(9)	72.95(8)
O(5)–Mo(1)–O(1)	96.6(1)	97.40(8)	95.79(9)
O(6)–Mo(1)–O(7)	82.3(1)	83.86(8)	85.04(8)
N(1)–Mo(1)–O(7)	71.76(8)	73.97(6)	71.31(7)
N(1)–Mo(1)–O(5)	100.5(1)	97.40(8)	99.06(9)
O(5)–Mo(1)–O(7)	172.0(1)	171.37(8)	170.36(9)
N(1)–Mo(1)–O(6)	153.9(1)	157.58(8)	156.35(9)

the *cis*-MoO_2 moiety [21,22]. A relationship between the basicity of the *O*-donor neutral ligand and the separation of the $\nu(MoO_2)$ bands (the higher the basicity the lower the separation) is also appreciated, but a definite explanation for this effect is not attempted since the differences in bond lengths and angles for the group *cis*-MoO_2 are not significant (see Table 2). The stretching bands for O–C, O–S and O–P of the coordinated ligands in complexes with DMF, DMSO, HMPA and $OPPh_3$ occur at 1637, 1081, 1154 and 1192 cm^{-1} respectively; they are shifted 20–25 cm^{-1} to lower wavenumbers with respect to those of the free ligands, which is indicative of coordination through the oxygen atom [23].

The ^1H NMR spectra of MoO_2(dipic)(L) (L = DMF, DMSO, HMPA and $OPPh_3$) are in agreement with those expected for octahedral complexes having a reflection plane and free rotation around the molybdenum-neutral ligand bond. The presence of two singlets for the methyl groups in MoO_2(dipic)(DMF) indicates that no free rotation exists around the C–N bond.

3.2. Molecular structures

Single-crystal X-ray diffraction studies on MoO_2(dipic)(L) (L = DMF, DMSO, $OPPh_3$) revealed that the three complexes have a closely related structure, similar to that of MoO_2(dipic)(DMF) shown in Fig. 1.

The molybdenum atom adopts the expected distorted octahedral geometry, which is determined by the usual way of coordination for the dipicolinate ligand (planar tridentate) to the angular *cis*-MoO_2 moiety.

Selected bond lengths and angles are listed in Table 2. The bond lengths for Mo–O(5) and Mo–O(6) are not identical, the former being shorter. While the Mo–O(6) distance, involving the oxygen *trans* to N(1), is nearly identical for all the complexes, the Mo–O(5) distance increases with the basicity of the *trans* ligand.

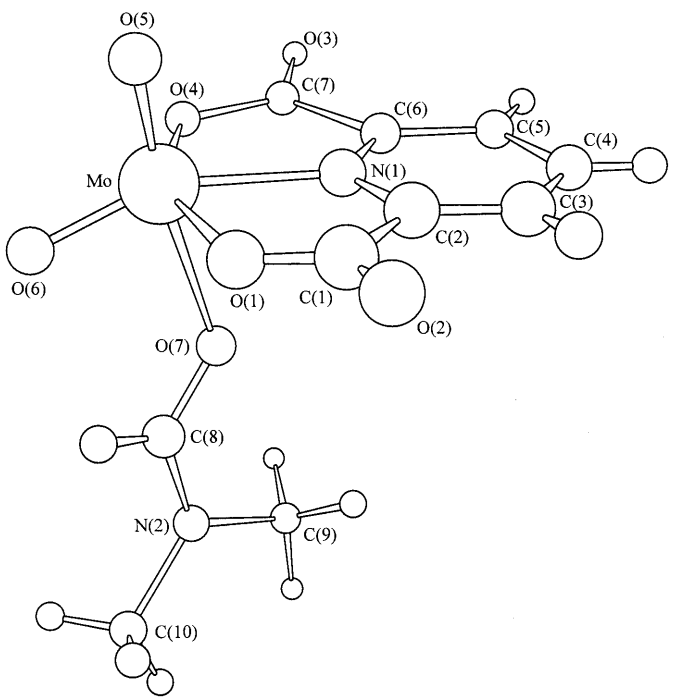

Fig. 1. Molecular structure and atom-labeling for complex MoO_2(dipic)(DMF); the hydrogen atoms are shown with small arbitrary radii.

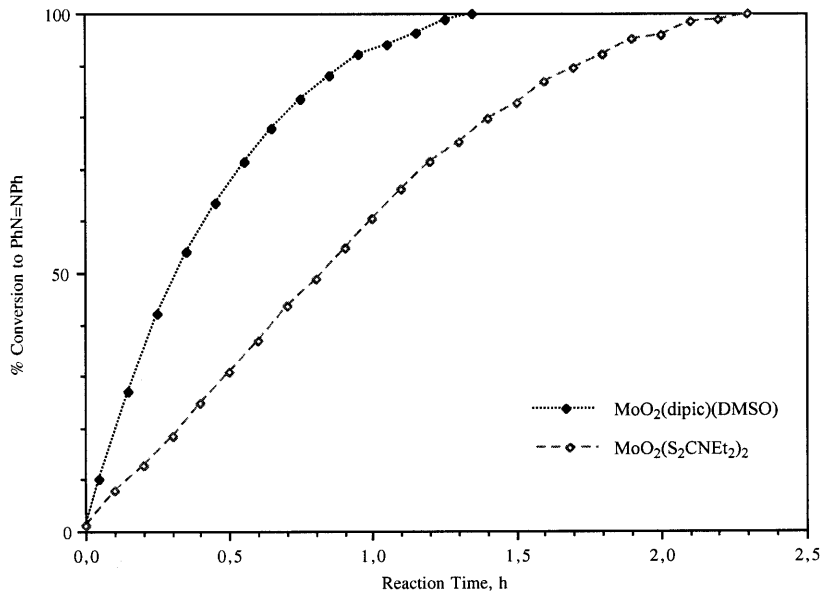

Fig. 2. Reduction of PhN(O)=NPh to PhN=NPh using PPh_3 as a funtion of time at [Mo] = 1.25 10^{-3} mol dm^{-3} and $[PPh_3]_0/[PhN(O)=NPh]_0/[Mo^{VI}]_0 = 10/1/0.05$.

The angles for the *cis*-MoO_2 group, O(5)–Mo–O(6), are very similar in the three compounds (ca. 105°), and in good agreement with those found for analogous complexes with *N*- and *O*-coordinated ligands [1,24].

3.3. Oxotransfer reactions

The oxygen atom transfer from MoO_2(dipic)(L) (L = DMF, DMSO, HMPA, $OPPh_3$) to PPh_3 has been examined. By treating acetone solutions of the complexes with PPh_3 a brown solution results at the same time that $OPPh_3$ forms. No significant difference in the behavior of the complexes MoO_2(dipic)(DMF), MoO_2(dipic)(DMSO) and MoO_2(dipic)($OPPh_3$) was observed, except for the evolution of the foul-smelling dimethyl sulfide (DMS) when the DMSO adduct was used. The only molybdenum product we could characterize, even in a large excess of PPh_3, is $Mo_2^{V}O_3$(dipic)$_2$($OPPh_3$)$_2$. Attempts to grow crystals suitable for X-ray characterization have been unsuccessful to date. Evidence — based on the ^{1}H NMR of the product — about formation of $Mo_2^{V}O_3$(dipic)$_2$(HMPA)$_2$ was found when using MoO_2(dipic)(HMPA), presumably due to the superior coordinating ability of HMPA with respect to $OPPh_3$. These results strongly suggest that: (i) $Mo^{IV}O$(dipic)(L) comproportionates as it forms with the remaining $Mo^{VI}O_2$(dipic)(L), at the same time that the coordinated DMF or DMSO are displaced by the $OPPh_3$ produced, thus leading to the dinuclear complex $Mo_2^{V}O_3$(dipic)$_2$($OPPh_3$)$_2$ which is very resistant to reduction; (ii) $Mo^{IV}O$(dipic)(DMSO) rearranges to $Mo^{VI}O_2$(dipic)(DMS) (PPh_3 is unable to deoxygenate DMSO in absence of MoO_2(dipic)(L) in the same conditions) and the resulting, soft ligand dimethyl sulfide is easily displaced from the coordination sphere of molybdenum. After this, it becomes evident that at least MoO_2(dipic)(DMSO) displays catalytic activity in oxotransfer reactions.

The catalytic activity of MoO_2(dipic)(DMSO) in the oxotransfer from DMSO to PPh_3 has been measured and compared with that of the prototypical $MoO_2(Et_2dtc)_2$ by following the formation of $OPPh_3$ by ^{31}P NMR as previously reported [13]. At 25°C the dithiocarbamate complex showed to be considerably more active than MoO_2(dipic)(DMSO). However, while $MoO_2(Et_2dtc)_2$ decomposes slowly in DMSO at room temperature, MoO_2(dipic)(DMSO) retains its catalytic activity for several days, as shown by addition of new batches of PPh_3 to the original solution.

The oxotransfer from azoxybenzene to PPh_3 has also been examined. Azoxybenzene derivatives are difficult to deoxygenate [25], and because of the low basicity of the azoxy group a weak coordinating solvent is advisable to avoid competition for the molybdenum center.

Fig. 2 shows the transformation of azoxybenzene into azobenzene with a large excess of PPh_3 in hot toluene in presence of $MoO_2(Et_2dtc)_2$ and MoO_2(dipic)(DMSO). The behavior of MoO_2(dipic)(DMF), MoO_2(dipic)(HMPA) and MoO_2(dipic)($OPPh_3$) is closely similar to that of MoO_2(dipic)(DMSO) and the results are omitted for clarity.

After completion of the deoxygenation process, $Mo_2O_3(Et_2dtc)_4$ and $Mo_2^{V}O_3$(dipic)$_2$($OPPh_3$)$_2$ could be isolated. The fact that we were unable to isolate oxomolybdenum(IV) complexes in a large excess of PPh_3 suggests that $Mo_2O_3(Et_2dtc)_4$ and $Mo_2^{V}O_3$(dipic)$_2$($OPPh_3$)$_2$ are the prevalent species in toluene solution, and that the equilibrium represented below — as well

as the analogous for $Mo_2O_3(Et_2dtc)_4$ — is strongly displaced to the left in poor coordinating solvents.

$$Mo_2O_3(dipic)_2(OPPh_3)_2 \leftrightharpoons MoO_2(dipic)(OPPh_3) + MoO(dipic)(OPPh_3)$$

4. Conclusions

(i) A number of air stable dioxomolybdenum(VI) dipicolinates can be easily prepared in good yields by reacting the readily available DMF or DMSO adducts of MoO_2Cl_2 with Na_2dipic, followed by addition of the appropriate ligand. (ii) The compounds, while showing a low catalytic activity in oxotransfer reactions at ambient temperature, display a high activity above 100°C which combined with the thermal stability of the complexes can be exploited in deoxygenation processes otherwise difficult to achieve.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 137435 {for [MoO_2(dipic)(DMF)]}, 137436 {for [MoO_2(dipic)(DMSO)]} and 137437 {for [MoO_2(dipic)($OPPh_3$)]}. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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