Camphor-based β -hydroxyphosphoryl ligands and their complexes of the type [MoO(O₂)₂L(H₂O)]

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Downloaded by University of Sussex on 04 October 2012 Published on 01 January 1996 on http://pubs.rsc.org | doi:10.1039/DT9960004149 Homochiral hydroxyphosphoryl compounds, L, such as the novel camphor-based (1R)-endo, endo-3S-(diphenyl-phosphoryl)-2R-hydroxybornane, have been found to be prevented from behaving as bidentate ligands in the epoxidation catalysts [MoO(O₂)₂L(H₂O)] by unexpectedly strong multiple-bond delocalisation producing near linear Mo-O-P angles.

Molybdenum(vI) oxoperoxo complexes $[MoO(O_2)_2L_2]$ are well established systems for the oxidation of organic substrates, notably alkenes.¹ The use of chiral ligands can lead to these complexes producing enantiomerically enriched products from prochiral starting materials,² particularly when bidentate ligands of high rigidity are employed.^{2,3} Chiral β -oxohydroxy ligands have been particularly successful in this respect.⁴ We have recently shown that chiral phosphorylhydroxy compounds are very versatile ligands for high-oxidation-level transition metals, including molybdenum(vI).^{5,6} We have therefore synthesized the new, chiral, camphor-based β -phosphorylhydroxy compounds L¹ and L² (Scheme 1) and examined their ligand behaviour towards the MoO(O₂)₂ fragment.

The known, slow $exo \longrightarrow endo$ interconversion of the intermediate phosphinoketones in solution⁷ allowed the isolation of both isomers from modifications of a single procedure. The products were obtained from the phosphinoketones by stereoselective reduction by LiAlH₄ to the hydroxyphosphines, followed by oxidation of the phosphine to the phosphine oxides with H₂O₂. The two isomers have quite distinct spectroscopic properties.*

Reaction of ethanolic solutions of L^1 or L^2 with $[MoO(O_2)_2(H_2O)_x]$ led to the isolation of yellow $[MoO(O_2)_2L(H_2O)]$ complexes.[†] The L^2 complex crystallised

readily from the reaction mixture giving X-ray-quality plates. The L¹ analogue was recovered as a slightly impure yellow powder by concentration of the reaction mixture and precipitation with diethyl ether. The contaminant appeared to be the ketophosphoryl, probably produced at the H_2O_2 oxidation step.

The structure of $[MoO(O_2)_2L^2(H_2O)]$ is shown in Fig. 1.‡ The co-ordination about the Mo^{VI} is the expected distorted pentagonal bipyramid common to complexes of this type, with the peroxo groups and the P=O oxygen of L² occupying the equatorial sites. Surprisingly, the ligand is monodentate, with an unbound hydroxy group. The co-ordination site opposite the oxo group is occupied by a water molecule. A further water molecule (centred on the unique C_2 crystallographic axis) is incorporated in the crystal lattice forming hydrogen bonds to the bound waters of two adjacent complexes. The hydroxide group of co-ordinated L² is not hydrogen bonded to any other unit, and the failure of this ligand to co-ordinate in a bidentate mode was quite unexpected.

The Mo–O(P) bond length at 2.013(3) Å is, to our knowledge, the shortest reported (cf. 2.085⁹ and 2.057 Å¹⁰ in related



Scheme 1 (i) LiBu, PPh₂Cl, tetrahydrofuran (thf); (ii) LiAlH₄, then H_2O_2 , thf

‡ Crystal data: $C_{22}H_{30}MOO_{8.5}P$, M = 557.37, yellow plates, crystal dimensions $0.37 \times 0.37 \times 0.10$ mm, orthorhombic, space group $P22_{1}2_{1}$, a = 8.0214(6), b = 16.0189(7), c = 18.5983(9) Å, U = 2389.8(2)Å³, Z = 4, $D_c = 1.549$ g cm⁻³, Mo-Ka radiation (graphite monochromator), $\lambda = 0.71073$ Å, F(000) = 1148,3333 observed reflections collected on an Enraf-Nonius Turbo CAD4 diffractometer. The structure was solved by direct methods and subsequent electron-density difference synthesis and refined by full-matrix least squares based on F^2 (SHELXL 93⁸) using 3079 absorption (ψ scans)-corrected data. The O-H atoms were found from Fourier-difference maps; the C-H atoms were included in calculated positions (C-H = 0.96 Å). The final R1 and wR2 $[I > 2\sigma(I)]$ were 0.0280 and 0.0669 for 299 parameters using the weighting scheme $w = [\sigma^2(F_o^2) + (0.0404 P)^2 + 0.4463 P]^{-1}$, where $P = F_o^2/3 + 2F_c^2/3$. A water molecule of crystallisation was found, sited on the crystallographic two-fold axis (i.e. occupancy 0.5). One of the hydrogen atoms of the ligated water molecule [O(7)] was disordered (0.75:0.25). Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, J. Chem. Soc., Dalton Trans., 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/286.

^{*} Found for L¹: C, 74.1; H, 8.0. Found for L²: C, 74.7; H, 7.8. Calc. for $C_{22}H_{27}O_2P$: C, 74.55; H, 7.70%. Spectroscopic data: L¹, NMR (CDCl₃), ¹H, δ 5.00 (br, 1 H), 4.36 (t, 1 H), 3.02 (m, 1 H), 2.24 (m, 1 H), 2.03 (m, 1 H), 1.62 (t, 1 H), 1.37 (m, 2 H), 0.89 (s, 3 H), 0.87 (s, 3 H) and 0.83 (s, 3 H); ³¹P, δ 33.8; IR (KBr) 3330 (OH), 1157, 1155 cm⁻¹ (P=O); L², NMR (CDCl₃), ¹H, δ 4.03 (dd, 1 H), 3.62 (br, 1 H), 2.65 (dd, 1 H), 1.94 (dd, 1 H), 1.75 (m, 2 H), 1.31 (s, 3 H), 1.10 (m, 2 H), 0.95 (s, 3 H) and 0.76 (s, 3 H); ³¹P, δ 38.0; IR (KBr) 3333, 3269 (OH), 1198, 1186 cm⁻¹ (P=O).

[†] The oxide MoO₃ (0.200 g, 1.39 mmol) was suspended in 30% H₂O₂ (4 cm³) and the mixture held at 45 °C for 4 h. After cooling, the solution was filtered into a solution of L¹ or L² (0.5 g, 1.4 mmol) in EtOH (10 cm³). The complex [MoO(O₂)₂L²(H₂O)]-0.5H₂O was isolated as yellow crystals (77% yield) after leaving overnight (Found: C, 47.2; H, 5.3. Calc. for C₂₂H₃₀MoO_{8.5}P: C, 47.40; H, 5.45%). NMR [(CD₃)₂CO]: ¹H, δ 4.66 (t, 1 H), 3.82 (br, 1 H), 3.45 (br, 1 H), 2.17 (m, 2 H), 1.80 (t, 1 H), 1.57 (m, 1 H), 1.21 (m, 1 H), 0.91 (s, 3 H), 0.88 (s, 3 H) and 0.83 (s, 3 H); ³¹P, δ 64.7; IR (KBr) 3486 (OH), 1142 (P=O), 970 (Mo=O), 876, 868 cm⁻¹ (O–O). The complex [MoO(O₂)₂L¹(H₂O)] was isolated as a yellow powder after concentration *in vacuo* at <20 °C (90% yield): elemental analyses revealed variable hydration and/or lattice ethanol (Found: C, 46.7; H, 6.0. Calc. for C₂₄H₃₇MoO₁₀P: C, 47.05; H, 6.10%). NMR (CDCl₃): (methyls only) δ 0.94, 0.89, 0.79, 0.65 and 0.39; ³¹P, δ 57.6; IR (KBr) 1119 (P=O), 974 (Mo=O), 875, 871 cm⁻¹ (O–O).



Table 1 The ${}^{31}P$ NMR data for complexes of the type [MoO(O₂)₂L(H₂O)] recorded in CDCl₃

P-Containing ligand	δ		
	Ligand	Complex	Δδ/ppm
R-Ph ₂ P(O)CH ₂ CHPh(OH) ⁵	33.9	56.0	22.1
S-Ph ₂ P(O)CH ₂ CHMe(OH) ⁵	34.0	55.8	21.8
S-Ph_P(O)CHMeCH_(OH) ⁵	39.6	61.9	22.3
S-L'*6	30.9	59.0	28.1
L ²	38.0	61.0	23.0
L ¹	33.8	57.6	23.8
* $L' = 2$ -Diphenylphosphoryl-	2'-hydroxy-1	,1'-dinaphthale	ne.

complexes), suggesting appreciable M–O double-bond character. This is supported by the almost linear P–O–Mo angle (171.0°). Burford *et al.*¹¹ have discussed the relation between bond lengths and angles and the extent of p_{π} – d_{π} type conjugate bonding in phosphine oxide complexes. They proposed that relatively extensive M=O=P bonding occurred in compounds where the P–O–M linkages approached linearity. It should be noted, however, that although a P–O–M bond linearity similar to that in our structure is observed in [MoO(O₂)₂{P(NMe₃)₃-O}(H₂O)],¹⁰ the coincident shortening of the Mo–O(P) bond was not apparent there.

The inability to isolate the desired $[MoO(O_2)_2L^2]$ containing bidentate L^2 was unexpected.¹² Molecular models reveal no adverse steric or geometric constraints on chelate

formation if a P–O–Mo angle of approximately 120–140° every adopted. Such chelate-ring formation would necessarily disrupt the near linear P–O–Mo linkage, however, and reduce the π bonding at the metal. Since the isolation of monodentate $[MoO(O_2)_2L^2(H_2O)]$ is not the consequence of steric hindrance, and is not encouraged by the formation of favourable hydrogen bonds (the non-co-ordinated OH function of the ligand is distant from all possible sources of intra- and inter-molecular hydrogen bonds), the π -bonding effect must dominate in this system. The ¹H NMR spectrum of $[MoO(O_2)_2L^2(H_2O)]$ allows unambiguous detection of the coordinated water, and confirms that bidentate co-ordination does not occur in solution either.

The ³¹P NMR spectrum of $[MoO(O_2)_2L^2(H_2O)]$ reveals an extremely large chemical shift from that of the uncomplexed hydroxyphosphoryl compound. This shift of 23 ppm is comparable to that caused by protonation at the phosphoryl oxygen¹¹ and is further evidence for the delocalisation of the P=O π -bond electron density over the Mo–O bond. We have synthesized several other complexes containing potentially bidentate hydroxyphosphoryl ligands attached to $MoO(O_2)_2$. All retain H₂O in their co-ordination spheres and all reveal similar, large shifts in $\delta(P)$ upon co-ordination, including $[MoO(O_2)_2L^1(H_2O)]$ (see Table 1). These values compare with shifts of only 1-14 ppm for complexes of Mo^{VI}, Zr^{IV} and Ti^{IV} in which the ligands are bidentate.^{5,6} The clear implication is that strong Mo–O–P π -bond delocalisation is a general phenomenon in these $[MoO(O_2)_2L(H_2O)]$ compounds, producing near linear Mo-O-P bond angles which prevent chelate formation in a way that reduces their efficacy as chiral oxidation catalysts.

Acknowledgements

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