The First Chelating Phosphorus–Nitrogen Dioxo Ligand: Complexation of an MoO(O₂)₂ Fragment

$$\text{The First Chelating Phosphorus–Nitrogen Dioxo Ligand: Complexation of an MoO(O_2)_2 Fragment}$$

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2-Diphenylphosphinoyl-N,N-dimethylaniline is oxidized at nitrogen by a dilute solution of H_2O_2 in the presence of $MoO(O_2)_2 \cdot (H_2O)_x$; the resulting phosphorus–nitrogen dioxo-ligand forms a molybdenum oxobisperoxo complex, which is structurally characterized by single crystal X-ray diffraction.

Seven-coordinate molybdenum peroxo complexes of the type $(L)_2MO(O_2)_2$ (L = monodentate ligand, M = Mo, W) and (L–L)MO(O₂)₂ (L–L = chelate ligand, M = Mo, W) are widely used as catalysts in olefin epoxidation.[1] The development of these homogeneous catalysts has its origin in a publication of Mimoun where the simple formation of complexes of the type $(L)_2MO(O_2)_2$ (M = Mo, W; L = HMPA, H_2O, DMF, C_5H_5N, C_5H_5N–O) is described.[2]

We are interested in ligand design for adapting catalysts to different solvent systems[3] and are looking for new combinations of donor groups in chelate ligands. Ligand development, especially with regard to the variation and control of steric and electronic properties of the donor moieties, is one basic conditions for the 'design' of new homogeneous catalysts. As the complexation of a metal fragment by a chelating phosphine oxide–amine oxide ligand is not yet known, we decided to investigate the reaction of 2-diphenylphosphinoyl-N,N-dimethylaniline 1 with a peroxidic solution of molybdic acid $MoO_3 \cdot (H_2O)_x$. Compound 1 is available from o-bromoaniline in a four-step synthesis. Methylation of o-bromoaniline with dimethyl sulfate under basic conditions at room temperature gave o-bromo-N,N-dimethylaniline[4] in 60% yield, lithiation of which in diethyl ether (1 h, reflux),[4] followed by addition of chlorodiphenylphosphine, gave (o-N,N-dimethylaminophenyl)diphenylphosphine in 83% yield.[4] Oxidation at phosphorus with H_2O_2 in THF led to 1† quantitatively.[4]

The reaction of a solution of excess $MoO(O_2) \cdot (H_2O)_x$, from H_2MoO_4 (6.22 mmol) in 30% H_2O_2 (25 ml), with a solution of 1 (3.11 mmol) in methanol (50 ml) did not lead to a P(O),N-chelate complex. After keeping this solution for several days at room temperature, yellow crystals had formed. The X-ray structure analysis of this compound showed the N-oxidized derivative 2 (Scheme 1), the first example of a complex containing a chelating phosphorus–nitrogen dioxo ligand.‡

The Mo^{VI} centre of 2 is coordinated by seven oxygen atoms (Fig. 1). It shows a distorted trigonal bipyramidal coordination geometry, if the η²-peroxo ligands are considered to occupy one equatorial coordination site. The axial positions are occupied by the oxo ligand and the N-oxide moiety of the chelate system.
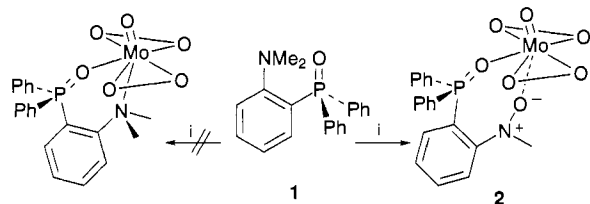
The distances and angles given in Fig. 1 correspond with data for other seven-coordinate molybdenum oxobisperoxo complexes.[5] Owing to the *trans*-influence of the axial oxo ligand, the bond distance Mo(1)–O(7) [2.330(2) Å] is longer than Mo(1)–O(1) [2.085(2) Å] though an N-oxide is a better donor compared to a phosphine oxide. Both distances are typical for phosphine oxide donors in equatorial positions and N-oxide donors in axial positions of $(L)_2MO(O_2)_2$ complexes. A CSD search[6] showed only one X-ray structure of a molecule

containing a chelating aliphatic N-oxide.[7] The structural data of the N-oxide moiety of 2 lie within the range of data of known structures. N–O distances of 1.365–1.470 Å and N–C distances of 1.432–1.529 Å [2: N–C, 1.488(4)–1.513(4) Å] have been observed. The bond angles Mo–O–N range from 113.6° to 141.5° depending on the steric demand of the other ligands on the metal. Only few X-ray structures with chelating aromatic phosphine oxides are known.[8] The observed P–O distance in 2 (Fig. 1) fits quite well with literature data (1.480–1.527 Å). The M–O–P angles of chelating phosphine oxides strongly depend on the size of the chelate ring system (five-membered ring: 114.5–116.2°; six-membered ring: 130.6–134.9°), while monodentate phosphine oxides prefer a more linear coordination (142.9–165.7°).[9] The aromatic backbone of the P,N-dioxo-ligand of 2, which is part of a seven-membered ring system, leads to a Mo(1)–O(1)–P(1) angle of 129.5(1)°.

The fact that 1 does not form a stable molybdenum peroxo complex can be explained by the reduced electron density of the nitrogen atom: The phosphine oxide in an *ortho*-position is a strongly electron-withdrawing substituent (Scheme 2).

The direct formation of the dioxo complex from the amine is not unusual. Even dilute solutions of H_2O_2 are able to oxidize amines. The corresponding N,N-dimethylaniline N-oxide has been known for almost 100 years.[10]

Complex 2 is insoluble in all common solvents and therefore can be characterized only by its solid-state data (IR spectrum, elemental analysis, X-ray structure analysis).§ Its insolubility prevents the application of 2 as a catalyst in homogeneous olefin epoxidation. We are now going to apply a strategy we developed for pyrazolylpyridine, a chelate ligand which also forms an insoluble molybdenum peroxo complex. Derivatisa-
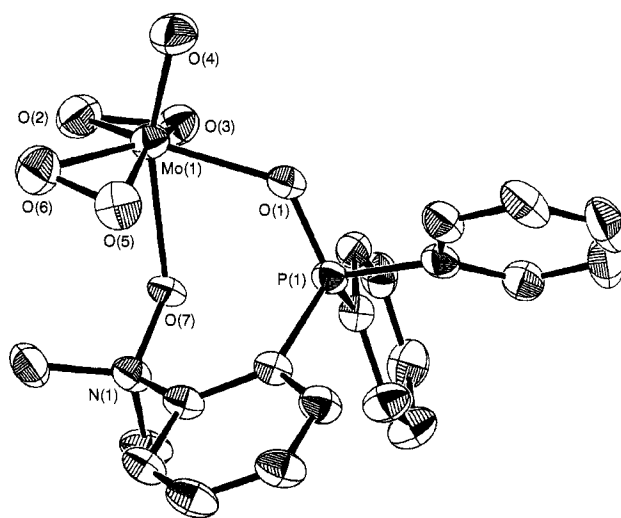

Fig. 1 X-Ray structure of 2. Selected distances (Å) and angles (°): Mo(1)–O(1) 2.085(2), Mo(1)–O(2) 1.907(2), Mo(1)–O(3) 1.948(2), Mo(1)–O(4) 1.682(2), Mo(1)–O(5) 1.949(2), Mo(1)–O(6) 1.904(2), Mo(1)–O(7) 2.330(2), O(1)–P(1) 1.524(2), O(2)–O(3) 1.475(3), O(5)–O(6) 1.480(3), O(7)–N(1) 1.399(3); O(1)–Mo(1)–O(4) 90.5(1), O(1)–Mo(1)–O(7) 71.72(7), O(4)–Mo(1)–O(7) 161.7(1), Mo(1)–O(1)–P(1) 129.5(1), Mo(1)–O(7)–N(1) 129.4(2), O(4)–Mo(1)–O$_{\text{Peroxo}}$ ca. 101.8

Scheme 1 *Reagents and conditions* i, H_2MoO_4, H_2O_2, MeOH, 20 °C

Scheme 2

tion with long alkyl chains leads to soluble complexes, which are efficient catalysts for the epoxidation of olefins in isooctane or toluene solution.[3] The synthetic route to **1** allows the introduction of long alkyl chains on nitrogen and/or phosphorus (Scheme 1) as well as the introduction of chiral substituents on these atoms. These chiral ligands should give chiral peroxo complexes, which are of interest for enantioselective olefin epoxidation. Direct N-oxidation of **1**, with H_2O_2–glacial acetic acid, should lead to the free phosphorus–nitrogen dioxo-ligand, a new chelating system which might coordinate to a broad variety of other high-valent transition or main group element fragments.

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Footnotes

† For **1**: satisfactory elemental analysis and spectroscopic data; ^{31}P NMR ($CDCl_3$) δ 25.7; IR v/cm^{-1} (KBr) 1192 (P=O); mp 139 °C; MS (EI, 70 eV) *m/z* (%) 321 (31) [M⁺], 306 (34) [M⁺ − CH_3], 291 (39) [M⁺ − C_2H_6], 230 (100) [M⁺ − C_7H_7], 199 (55) [M⁺ − $C_6H_5NMe_2$], 183 (40) [M⁺ − $C_6H_5NMe_2$ − O], 152 (44) [P–$C_6H_4NMe_2$ + H⁺], 91 (68) [C_7H_7⁺], 77 (72) [C_6H_5⁺].
‡ *Crystal data* for **2**: $C_{20}H_{20}MoNO_7P$, M = 513.3 yellow prisms, triclinic, $P\bar{1}$, a = 8.262(2), b = 10.584(3), c = 12.804(4) Å, α = 111.76(1), β = 93.23(2), γ = 90.50(2)°, V = 1038 Å³, Z = 2, D_c = 1.643 g cm^{-3}, T = 223 K, Mo-Kα radiation (graphite monochromator), λ = 0.71073 Å, μ = 7.5 cm^{-1}, $F(000)$ = 520, 12 071 observed reflections collected on a Stoe IPDS, 3075 independent reflections, 2993 reflections with I > $0.01\sigma(I)$ used for refinement, LP corrections applied. The structure was solved by the Patterson method and refined with difference-Fourier techniques, protons

were located from difference-Fourier maps and refined with isotropic thermal parameters. Refinement converged with R = 0.034 and R_w = 0.028. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.
§ For **2**: satisfactory elemental analysis; IR v/cm^{-1} (KBr) 951 (Mo=O), 862 (O–O).

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