

Multiple bonds between main group elements and transition metals, 155¹.

(Hexamethylphosphoramide) methyl(oxo)bis(η^2 -peroxo)rhenium(VII), the first example of an anhydrous rhenium peroxo complex: crystal structure and catalytic properties²

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Abstract

Methyl(oxo)bis(η^2 -peroxo)rhenium(VII) **1**, the active species of the system $\text{CH}_3\text{ReO}_3/\text{H}_2\text{O}_2$ in the catalytic oxidation of different organic and organometallic compounds, is stabilized by a water molecule attached to the rhenium center. This water molecule can be removed and substituted by hexamethylphosphoramide (HMPA) to yield (hexamethylphosphoramide)methyl(oxo)bis(η^2 -peroxo)rhenium(VII) (**3**). The synthesis, crystal structure (X-ray diffraction study), and catalytic properties of which compound are reported. Crystal data are as follows: monoclinic, space group $P2_1/n$, $a = 900.76(7)$ pm, $b = 1229.80(11)$ pm, $c = 1318.57(11)$ pm, $\beta = 90.251(7)^\circ$, $R_w = 0.034$ for 1878 reflections. The catalytic properties of compound **3** in the oxidation of olefins with H_2O_2 are similar to those of **1**.

Keywords: Rhenium; Methyl(oxo)bis(η^2 -peroxo)rhenium(VII); Crystal structure

1. Introduction

The bis(peroxo)rhenium(VII) complex $\text{CH}_3\text{ReO}(\text{O}_2)_2 \cdot \text{H}_2\text{O}$ (**1**), the catalytic active species of the system $\text{CH}_3\text{ReO}_3/\text{H}_2\text{O}_2$, was isolated and structurally fully characterized [2a,3a] in an earlier study from our laboratory. This complex is the intermediate responsible for the catalytic oxidation of alkenes [3] and alkynes [4], aromatic compounds [5], organic sulfides [6], phosphines, triphenylarsine and triphenylstibine [7], tertiary amines [8] and for the *Baeyer–Villiger* oxidation [9].

Owing to the metal Lewis-acidity of the peroxo complex **1** (Re^{VII}) and the aqueous conditions of its preparation, a water molecule is attached to the rhenium center. A fast exchange process of this water molecule can be observed by ^{17}O -NMR spectroscopy in solution, indicating that the $\text{Re}-\text{OH}_2$ bond may be weaker than initially predicted [3a].

Interestingly, the first inorganic binuclear peroxo complex of Re^{VII} , $\text{O}[\text{Re}(\text{O}_2)_2\text{O}]_2 \cdot (\text{H}_2\text{O})_2$ (**2**) [5b], also exhibits coordinated water molecules. This complex is considered to be the catalytic active species of the system $\text{Re}_2\text{O}_7/\text{H}_2\text{O}_2$ in the oxidation of olefins, aromatic compounds, and metal carbonyl complexes [5b]. Unlike **1**, $\text{O}[\text{Re}(\text{O}_2)_2\text{O}]_2 \cdot (\text{H}_2\text{O})_2$ is highly sensitive to hydrolysis, affording the unreactive perrhenic acid ($\text{H}[\text{ReO}_4]$). For this reason, the binuclear complex **2** is not a catalyst in spite of the pronounced oxidative properties.

Now we describe the first water-free Re^{VI} peroxo complex in the solid phase [10a].

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¹ Ref. [1].

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2. Synthesis, structure, and spectroscopy

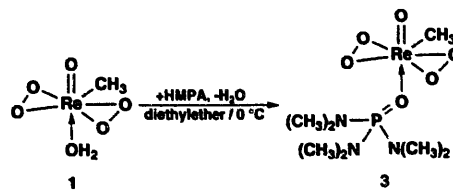
Hexamethylphosphoramide (HMPA) is often used to stabilize peroxy complexes of molybdenum and tungsten [10b]. Until now it has not been used in rhenium-containing systems, so the influence of this ligand on the catalytic properties of the system $\text{CH}_3\text{ReO}_3/\text{H}_2\text{O}_2$ is still unknown. Slow addition of dry HMPA to a yellow–orange ethereal solution of **1** at 0°C immediately affords **3** as orange crystals (Scheme 1).

The product is soluble in methylene chloride but, unlike **1**, it is insoluble in diethylether. It is also less hygroscopic, melts at $63\text{--}65^\circ\text{C}$ (decomp. $70\text{--}77^\circ\text{C}$) and can be handled under air for at least 1 h without decomposition. The IR spectrum in methylene chloride shows the absorption bands of the terminal oxo ligand ($\nu(\text{Re}=\text{O}) = 992\text{ cm}^{-1}$), the η^2 -peroxy groups (871 cm^{-1}), and a band corresponding to the coordinated HMPA molecule ($\text{Re}-\text{O}-\text{P}$, 1158 cm^{-1}). The latter is in the range normally observed for the interactions between $\text{P}=\text{O}$ and other different metals [11]. Bands corresponding to ReOOH groups are not observed.

The peroxy complex **3** reacts stoichiometrically with *cis*-cyclooctene in dry THF at room temperature, yielding quantitatively cyclooctene oxide in the same way as previously observed for **1** [3a]. This supports the presence of an intermediate containing η^2 -peroxy groups in the catalytic olefin oxidation mediated by $\text{H}_2\text{O}_2/\text{CH}_3\text{ReO}_3$.

To determine the solid-state structure of **3**, a single crystal X-ray analysis was performed (Fig. 1). The trigonal bipyramidal geometry of the complex is similar to that of compound **1** [3a]. All atom–atom distances within the $\text{CH}_3\text{Re}(\text{O})(\text{O}_2)_2$ fragment are almost identical, and the observed angles show no significant differences either. However, the distance $\text{Re1}-\text{O6}$ ($2.175(4)\text{ \AA}$) is significantly shorter than the distance $\text{Re}-\text{OH}_2$ in **1** ($2.253(4)\text{ \AA}$), reflecting the more pronounced donor quality of the phosphine oxide as compared with water, quite in accord with the IR and NMR experiments in solution: the IR spectrum of **3** in solution (CH_2Cl_2) shows a shift of the $\text{Re}=\text{O}$ band to shorter wavenumbers (992 cm^{-1}) compared with the $\text{Re}=\text{O}$ stretching band of the precursor compound **1** (1020 cm^{-1}).

In the ^{17}O -NMR spectra, the terminal oxo peak ($\text{Re}=\text{O}$) of **1** occurs at 760 ppm (CDCl_3 , -25°C),



Scheme 1.

while in **3** the same peak is shifted to lower field (774 ppm , CDCl_3 , -25°C). In fact, it is known that for complexes of the type $\text{CH}_3\text{ReO}_3 \cdot \text{L}$ ($\text{L} = \text{N-base}$), the more pronounced the donor properties of the ligand the lower field the terminal oxo peak is shifted [12]. This shift is obviously due to a higher electron density at the rhenium center.

In spite of the different geometries of the complexes $\text{CH}_3\text{ReO}_3 \cdot \text{L}$ (L *trans* to the CH_3 group) and $\text{CH}_3\text{Re}(\text{O})(\text{O}_2)_2 \cdot \text{L}$ ($\text{L} = \text{H}_2\text{O}$ or HMPA, L *trans* to the oxo group), the observed IR and ^{17}O -NMR shifts can be compared since the terminal oxo groups ($\text{Re}=\text{O}$) are in both cases influenced by the higher electron density at the rhenium center caused by the ligands [12a].

3. Catalysis

Use of a mixture of CH_3ReO_3 (1 mol%)/HMPA (6 mol%) as catalyst in the oxidation of cyclohexene with H_2O_2 in $^i\text{BuOH}$ (room temperature) leads to 100% conversion of the starting material, but surprisingly no epoxide is obtained. Instead, the oxirane ring is opened

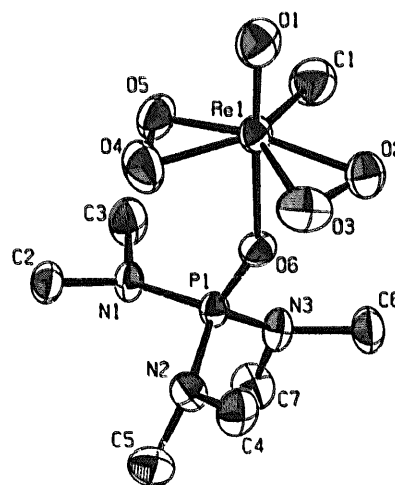
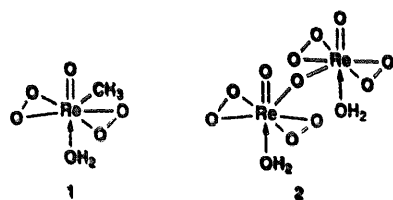


Fig. 1. Crystal and molecular structure of the peroxorhenium(VII) **3** [13]. Ellipsoids are drawn at 50% probability level, hydrogen atoms are omitted for clarity. Selected distances (\AA) and angles ($^\circ$): $\text{Re1}-\text{O1}$ $1.676(5)$, $\text{Re1}-\text{O2}$ $1.905(5)$, $\text{Re1}-\text{O3}$ $1.921(5)$, $\text{Re1}-\text{O4}$ $1.917(4)$, $\text{Re1}-\text{O5}$ $1.915(5)$, $\text{Re1}-\text{O6}$ $2.175(4)$, $\text{Re1}-\text{C1}$ $2.132(7)$, $\text{O2}-\text{O3}$ $1.463(7)$, $\text{O4}-\text{O5}$ $1.482(7)$, $\text{P1}-\text{O6}$ $1.487(4)$, $\text{O1}-\text{Re1}-\text{O6}$ $176.1(2)$, $\text{O1}-\text{Re1}-\text{C1}$ $93.6(3)$, $\text{O6}-\text{Re1}-\text{C1}$ $82.6(2)$, $\text{Re1}-\text{O6}-\text{P1}$ $149.5(3)$.

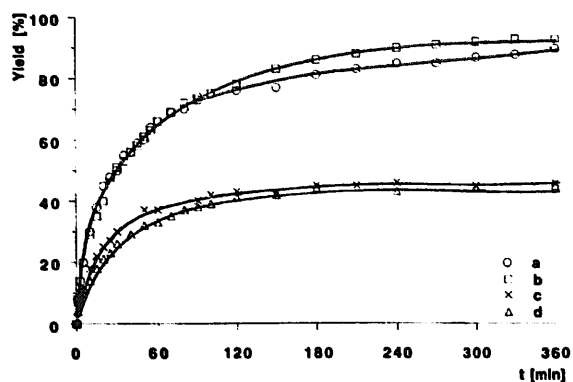


Fig. 2. Catalytic activity of CH_3ReO_3 (a, c), **3** (b), and $\text{CH}_3\text{ReO}_3/\text{HMPA}$ (d) in the oxidation of *cis*-cyclooctene to cyclooctene oxide with H_2O_2 . (a, b) *cis*-Cyclooctene: H_2O_2 : [cat.] 1:1.5:0.005; (c, d) *cis*-cyclooctene: H_2O_2 : [cat.]:HMPA (only in curve D) 1:1.5:0.003:0.015; $T = 25^\circ\text{C}$.

consecutively to form 1,2-dihydroxycyclohexane and 1-*t*-butoxy-2-hydroxycyclohexane, as in the case of CH_3ReO_3 .

Since HMPA does not seem to have any influence on the chemoselectivity of the system $\text{CH}_3\text{ReO}_3/\text{H}_2\text{O}_2$, we studied the epoxidation of *cis*-cyclooctene. For the sake of further comparison two sets of experiments were performed.

(a) The catalytic activity of CH_3ReO_3 ([cat.] ≈ 0.5 mol%) was compared with that of isolated **3** (curves a and b respectively in Fig. 2). The activities of the catalysts are not very different from each other.

(b) The catalytic activity of CH_3ReO_3 ([cat.] ≈ 0.3 mol%) was compared with that of the system CH_3ReO_3 (1 mol%)/HMPA (5 mol%) (curves c and d respectively in Fig. 2). As seen in Fig. 2, the HMPA ligand once again does not reveal any influence on the catalytic activity.

4. Conclusion

The oxidation catalysts of type $\text{CH}_3\text{ReO}_3 \cdot \text{S}$ ($\text{S} = \text{H}_2\text{O}$, HMPA) show an almost identical performance in the oxidation of olefins by means of hydrogen peroxide, in contrast to the results known for $\text{CH}_3\text{Re}(\text{O})(\text{O}_2)_2 \cdot \text{L}$ ($\text{L} = \text{N}$ -base, e.g. quinuclidine). This difference is likely to result from a faster exchange process of the solvent ligands H_2O and HMPA under catalytic conditions. Thus, the Lewis-acidity of the catalytic system is still high enough to allow the oxirane ring opening. As compared with the $\text{P}=\text{O}$ group of HMPA, the N -base ligands are the stronger donors at Re^{VII} and thus avoid the acid-catalyzed epoxide hydrolysis. At this moment we are concentrating our attention on the isolation and structural characterization of complexes of the type $\text{CH}_3\text{Re}(\text{O})(\text{O}_2)_2 \cdot \text{L}$ ($\text{L} = \text{N}$ -bases, N -oxides) as well as on their catalytic properties.

5. Experimental details

All reactions were performed with standard Schlenk techniques in oxygen-free and water-free nitrogen atmosphere. Solvents were dried with standard methods and distilled under N_2 . Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer (resolution 4 cm^{-1}); the ^1H - and ^{17}O -NMR spectra, at 399.78 and 54.21 MHz respectively, were recorded on an FT-JEOL GX 400 instrument. All NMR solvents were "freeze-pump-thaw" degassed and stored over molecular sieves before use. Elemental analyses were performed in the microanalytical laboratory of our institute. The catalytic reactions were monitored on a HP 5890 (GC) equipped with a fused-silica column (HP-1) (No. 19091Z-102, $l = 50 \text{ m}$, $\phi = 0.2 \text{ mm}$, thickness of film $0.33 \mu\text{m}$) as well as an FI-detector. Methy(oxo)bis(η^2 -peroxo)rhenium(VII) (**1**) was prepared according to Ref. [3a].

5.1. Preparation of (Hexamethylphosphoramide)methyl(oxo)-bis(η^2 -peroxo)rhenium(VII) (**3**)

0.59 g (2.2 mmol) of **1** was dissolved at 0°C under nitrogen atmosphere in 10 ml of dry diethylether. To the cooled (0°C) solution was added dropwise hexamethylphosphoramide (0.4 ml, approximately 2.2 mmol) dissolved in 2 ml of diethylether. A red-orange crystalline solid precipitated immediately. The remaining solvent was filtered and the solid washed with diethylether ($2 \times$) and *n*-pentane ($2 \times$). After drying under high vacuum, 0.902 g (1.96 mmol, 98%) of orange-reddish crystals of **3** was obtained. M.p. $63\text{--}65^\circ\text{C}$ (decomp. $70\text{--}77^\circ\text{C}$). IR (CH_2Cl_2): $\nu(\text{P}=\text{O}-\text{Re})$ 1158s, ($\text{P}-\text{N}-\text{C}$) 1069vw, ($\text{Re}=\text{O}$) 992vs, (O_2) 871s cm^{-1} . ^1H -NMR (400 MHz, CDCl_3 , 25°C): $\delta = 2.54$ (d, $J(\text{H,H}) = 10 \text{ Hz}$, 18H, $\text{N}(\text{CH}_3)_2$); 2.76 (s, 3H, $\text{Re}-\text{CH}_3$) ppm. ^{13}C -NMR (100.5 MHz, CDCl_3 , 25°C): $\delta = 30.62$ ($\text{Re}-\text{CH}_3$); 37.05 ($\text{N}(\text{CH}_3)_2$) ppm. ^{17}O -NMR (54.2 MHz, CDCl_3 , -20°C): $\delta = 774$ ($\text{Re}=\text{O}$) ppm. Anal. Found: C, 18.23; H, 4.65; N, 9.27; O, 21.47; Re, 39.19. $\text{C}_7\text{H}_{21}\text{N}_3\text{O}_6\text{PRe}$ (460.44) Calc.: C, 18.25; H, 4.60; N, 9.12; O, 20.84; Re, 40.44%.

5.2. X-ray structure determination of (Hexamethylphosphoramide)methyl(oxo)bis(η^2 -peroxo)rhenium(VII) (**3**)

A single crystal of deep orange colored **3** was prepared under air and mounted in a glass capillary on an image plate diffraction system (IPDS, STOE). Final lattice parameters were obtained by least-squares refinement of 1818 reflections with $I/\sigma(I) > 6$ (graphite monochromator, $\lambda = 71.073 \text{ pm}$, Mo $\text{K}\alpha$). Monoclinic system, space group $P2_1/n$ (International Tables, no. 14), $a = 900.76(7) \text{ pm}$, $b = 1229.80(11) \text{ pm}$, $c =$

1318.57(11) pm, $\beta = 90.251(7)^\circ$, $V = 1460.6 \times 10^6$ pm³, $\rho_{\text{calc}} = 2.09$ g cm⁻³, $Z = 4$. Data were collected at $-50(\pm 0.3)^\circ\text{C}$, distance from crystal to image plate 80 mm ($2.86^\circ < 2\theta < 48.4^\circ$), 101 images collected, $0^\circ < \varphi < 101^\circ$, $\Delta\varphi = 1^\circ$, exposure time 6 min per image. Data were corrected for Lorentz and polarization terms. 4524 data measured, 76 overflows, 0 overlaps, 54 reflections systematically absent, 4470 data merged, 1993 independent reflections, 115 with negative intensity, 1878 reflections with $I/\sigma(I) > 0$ used for refinement, Chebyshev weighting scheme [14]. The structure was solved by the Patterson method [15] and refined with standard difference Fourier techniques [15]. All hydrogen atoms could be found by difference Fourier maps, but they were not refined. 163 parameters refined, 11.5 data per parameter, residual electron density $+0.89$ e Å⁻³ 102 pm near Re, -0.73 e Å⁻³, $R = 0.034$, $R_w = 0.034$.

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-404777, the journal citation and the names of the authors.

5.3. Catalytic reactions

5.3.1. Preparation of oxidation solution (10% H₂O₂ in ^tBuOH)

^tBuOH (1 l) was maintained at 25–30°C and mixed with 0.1 l of 85% H₂O₂ in H₂O. The solution was stirred with anhydrous MgSO₄ (ca. 100 g) for 3 h and then filtered.

5.3.2. General procedure for catalytic oxidation

The catalyst (0.08–0.05 mmol) and dibutyl ether (1.94 g, internal standard) were dissolved in the oxidation solution (8.7 ml, 25 mmol H₂O₂). Free HMPA (0.035 ml, 0.25 mmol) was then added (only for curve d) and the temperature was maintained at $25 \pm 1^\circ\text{C}$. 2 g (17 mmol) of *cis*-cyclooctene was added. The reaction was monitored by GC using an FI-detector. The results are presented in Fig. 2.

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