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Synthesis, structural characterization and catalytic properties of a novel monomeric rhenium(V)methyl(oxo)bis(η^2-picolinato) complex: $[CH_3Re(O)(pic)_2]$ †

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A methyl mono-oxo rhenium(V) complex with two picolinato chelating ligands has been synthesized and structurally characterized. When reacted with excess 10 or 30% H_2O_2 it forms peroxo species responsible for the catalytic activity of a highly selective two-phase medium.

Rhenium heptaoxide, Re_2O_7, has been considered as a precursor for oxidations of alkenes with hydrogen peroxide; epoxides and/or ketones are formed and cyclododecene is oxidatively cleaved. Improvements in dihydroxy addition to C=C bonds (with diol yields up to 80%) and in oxidative olefin cleavage by "Re_2O_7/H_2O_2" (with carboxylic acid yields of 50–80%) have been reported.[1] An important improvement in this field arose with the discovery of a novel catalytic system: "methyltrioxorhenium (CH_3ReO_3)/H_2O_2–*t*-BuOH" which can be used for olefin epoxidation and hydroxylation.[2] The precursor CH_3ReO_3[3] (MTO) is expensive but can be recycled. Therefore, rhenium compounds should be studied as oxidation catalysts for synthetic purposes and compared to d^0 transition metal precursors, particularly to the molybdenum(VI) and tungsten(VI) analogues.[4] While studying oxidation reactions with hydrogen peroxide, d^0 species and assembling ($[PO_4]^{3-}$; $[HPO_4]^{2-}$; $[SO_4]^{2-}$; *etc.*) or chelating ligands (with phase transfer catalysis[4,5] or in a two-phase medium[4,6]), we became interested in establishing relationships between anionic or neutral peroxo complexes and the precursor or species formed without H_2O_2. Addition of pyridine derivatives to two-phase MTO systems gave epoxides selectively.[4,6–8] The bipyridine system was also used for the preparation of previously unknown epoxides.[6] Novel species isolated from the reaction media include the molecular complex $[CH_3Re(O)(pic)_2]$, (picH = 2-pyridinecarboxylic acid) which is the first Re(V) complex with a H_3C–Re=O moiety and is a new precursor for hydrogen peroxide oxidations.

MTO (0.06 g, 0.24 mmol) was added to an aqueous solution of picH (0.0885 g, 0.72 mmol). The solution was stirred for two or three days at room temperature, during which it gradually became yellow, then olive-green; a green microcrystalline powder was formed (yield ≈ 30%). This was washed with Et_2O and recrystallized from dichloromethane–*n*-hexane mixtures to give dark-green crystals of $[CH_3Re(O)(pic)_2]$ **1** suitable for X-ray analysis.‡

Irrespective of the exact nature of the intermediates, two of the three oxo ligands of MTO are labilized by the picolinato chelate. Metal–oxo complexes frequently undergo reduction by organophosphines, but less readily by amines. With CH_3ReO_3, a stoichiometric 1 : 1 or 1 : 2 reaction may occur to yield the picolinic acid *N*-oxide. No evidence was found for formation of the acid or picolinato *N*-oxide complexes. At the same time, competitive oxidation of the methyl group of MTO occurs, leading to $HReO_4$ characterized by precipitation of $[n\text{-}Bu_4N^+\text{-}ReO_4^-]$ (addition of an aqueous solution of $[n\text{-}Bu_4N^+HSO_4^-]$), and also by isolation of protonated picH in the form of single crystals of $[\{(picH_2)^+(picH)\}ReO_4^-]$. It is known[9] that MTO can be decomposed by nucleophilic attack in aqueous solutions as acidic as pH 2–3 by transient amine *N*-oxide or even by OH^- or a free radical process.

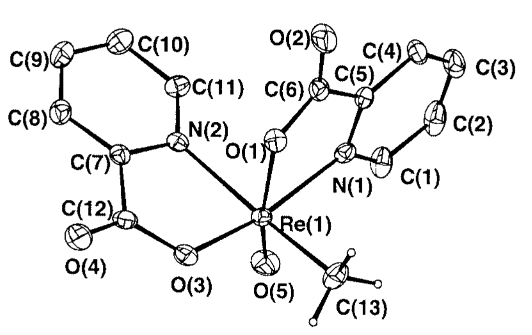

Fig. 1 CAMERON representation[12] of $[CH_3Re(O)(pic)_2]$ showing the atom labelling scheme. Ellipsoids represent 20% probability. Selected bond lengths (Å) and bond angles (°): Re(1)–O(1) 2.094(4), Re(1)–O(3) 2.003(4), Re(1)–O(5) 1.658(5), Re(1)–N(1) 2.097(5), Re(1)–N(2) 2.149(5), Re(1)–C(13) 2.128(7), O(1)–C(6) 1.283(8), O(2)–C(6) 1.204(8), O(3)–C(12) 1.329(8), O(4)–C(12) 1.198(8); O(1)–Re(1)–O(3) 85.3(2), O(1)–Re(1)–O(5) 164.6(2), O(3)–Re(1)–O(5) 109.9(2), O(1)–Re(1)–N(1) 74.4(2), O(3)–Re(1)–N(1) 159.7(2), O(5)–Re(1)–N(1) 90.4(2), O(1)–Re(1)–N(2) 76.2(2), O(3)–Re(1)–N(2) 78.3(2), O(5)–Re(1)–N(2) 103.8(2), N(1)–Re(1)–N(2) 97.8(2), O(1)–Re(1)–C(13) 83.5(3), O(3)–Re(1)–C(13) 87.9(2), O(5)–Re(1)–C(13) 99.1(3), N(1)–Re(1)–C(13) 88.5(3), N(2)–Re(1)–C(13) 156.1(3).

A representation of the molecular complex **1** is shown in Fig. 1. The monomeric, neutral and pseudo-octahedral dipicolinato complex **1** is formally a rhenium(V) species. The rhenium centre has a distorted octahedral environment consisting of four coordinated atoms of the two chelating ligands with *cis*-nitrogen and *cis*-oxygen configurations; one pic ligand is bridging an equatorial and an apical position and the other is bridging two equatorial sites. A carbon atom of the methyl group completes the equatorial plane.

A "twisted mode" is reflected in the N(1)–Re(1)–O(3) [159.7(2)], N(2)–Re(1)–C(13) [156.1(3)] and O(1)–Re(1)–O(5) [164.6(2)°] angles which deviate from 180° and in the position of the Re atom located 0.38 Å outside the mean equatorial plane defined by the N(1), N(2), O(3) and C(13) atoms. Comparison

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† Non-IUPAC nomenclature employed. Picolinato and the abbreviation (pic) are being used to represent the anion of 2-pyridinecarboxylic acid.

Table 1 A two-phase system: $[CH_3Re(O)(pic)_2]/H_2O_2–H_2O/CH_2Cl_2$ for epoxidation of acid-sensitive epoxides[a]

Substrate	Time/h	Temperature	Conversion (%)	Selectivity (%)
1-Octene	24	RT[e]	96	99[b]
Limonene	2	4 °C	94	93[c]
2-Methyl-3-buten-2-ol	24	RT[e]	92	99[d]

[a] Reaction conditions: olefin (6–10 mmol) in dichloromethane 5 ml, **1** (1 mol%/olefin), 10% H_2O_2 (aq.) (150 equivalents of H_2O_2 added with vigorous stirring). The progress of the reaction was monitored by GC and the products were analysed after quenching with MnO_2. [b] With "MTO/H_2O_2–*t*-BuOH/oct-1-ene" (homogeneous system): diol yield ≥70%,[2] depending on the acidity. [c] A nearly 1:1 mixture of the two isomeric monoepoxides (*cis* and *trans*).[5,6] [d] With the homogeneous system: epoxide yield 10%. [e] RT = room temperature.

of **1** and $[CH_3Re(O)(O_2)_2(HMPA)]$[10] shows that the Re=O and Re–C distances are unaffected by the oxidation number and the geometry about Re. The latter bond length (Re–C) compares well with the mean Re^{III}–C (2.086 ± 0.008 Å) in $K_4[Re(CN)_7]\cdot 2H_2O$ in which the cyanide is a π-acceptor.[11] It is inferred that the structure of the O=Re–CH_3 moiety does not change during the redox process, and the stabilization of a rhenium–carbon bond by one oxo ligand can be achieved not only with Re(VII), but also with Re(V).

The IR spectra of complex **1** show features comparable to those of mononuclear picolinato species; in addition to two strong bands at 1700 and 1679 cm^{-1}, assigned to $\nu(C=O)_{asym}$, there is a very sharp band at 1006 cm^{-1} [ν(Re=O)]; Re–C stretch appears at *ca.* 552–538 cm^{-1} (sh). Comparison of IR and Raman spectra and ^{13}C NMR in the solid state and CH_2Cl_2 solution suggests that the overall structure of the molecular species is conserved in solution.

The Re(V) complex is also an active precursor in olefin oxidation and forms epoxides in the range 4–20 °C (Table 1) in a two-phase "$H_2O_2–H_2O/CH_2Cl_2$" system. Several unidentified peroxo species are formed with characteristic Raman $\tilde{\nu}$(O–O) bands near 850 cm^{-1}; they transfer active oxygen to olefinic substrates, even to 2-methyl-3-buten-2-ol, a tertiary allylic alcohol which rearranges easily in the presence of alkoxides with Re(V) or Re(VII) precursors. Conversions and yields compare well with recent data in which MTO is used in place of **1**.

The activity of this rhenium-based two-phase system under mild conditions encourages further work to prepare analogues in the hope of finding novel precursors for oxidations by H_2O_2 and particularly of alkenes.

Notes and references

‡ Complex **1** gave satisfactory elemental analyses. Calc.: C, 33.84; H, 2.40; N, 6.07. Found for $C_{13}H_{11}N_2O_5Re$: C, 33.70; H, 2.20; N, 5.85%.

§ Crystal data and collection parameters:[13] $C_{13}H_{11}N_2O_5Re$ **1**, M = 461.44, monoclinic, space group $C2/c$ (no. 15), a = 28.339(7), b = 7.070(3), c = 15.124(3) Å, β = 111.75(2)°, U = 2814(2) Å^3, T = 293 K, graphite-monochromated Mo-Kα radiation, λ = 0.71069 Å, Z = 8, μ(Mo-Kα) = 87.7 cm^{-1}, $2 \le 2\theta \le 50°$, 2607 unique data collected of which 2072 with $(F_o)^2 > 3\sigma(F_o)^2$ were used in all calculations. Corrections were made for Lorentz and polarization effects, an extinction correction was also applied and empirical absorption correction on the basis of ψ-scan data was introduced before anisotropic refinement (min. 0.77, max. 1.69). Secondary extinction correction was necessary. Hydrogen atoms were found on difference maps; their positions were not refined and they were given an overall isotropic thermal parameter U_{iso} = 0.09(1). The final R factors as defined in ref. 12 were R = 0.033 and R_w = 0.041 for 190 parameters and weighting scheme, GOF = 1.11, maximum $\Delta\rho$ = 1.03 e Å^{-3}, minimum $\Delta\rho$ = −1.07 e Å^{-3}. CCDC reference number 186/1578. See http://www.rsc.org/suppdata/dt/1999/2897/ for crystallographic files in .cif format.

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