Bis(alkoxy)ruthenium(IV) Porphyrin Complexes and Aerobic Oxidation of Alcohols
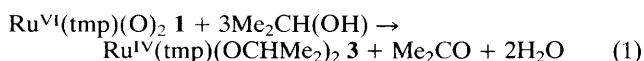
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The complex trans-Ru^{VI}(tmp)(O)$_2$ (tmp = dianion of 5,10,15,20-tetramesitylporphyrin) oxidizes alcohols via bis(alkoxy) species, of which the bis(isopropoxy) complex has been characterized crystallographically.

We have commented briefly on the reaction of trans-Ru^{VI}-(tmp)(O)$_2$ **1** with propan-2-ol (Pr^{i}OH) to generate acetone, water and an *in situ* species tentatively suggested to be trans-Ru^{IV}(tmp)(OH)$_2$ **2**, mainly because of non-detection of coordinated propoxide ligands and similarity to an isolated bis(phenoxy) complex.[1] Che's group, although not referring to our report, has more recently reported on characterization of **2**, including a mention of unpublished crystallographic data.[2] This latter paper prompts us to report our new data that show **2** is not formed *via* reaction of **1** with alcohols; the product is a bis(alkoxy) species. The findings are important because the supposed **2** affects catalytic aerobic epoxidation of alkenes and is more efficient than **1**, a genuine dioxygenase catalyst, under corresponding conditions.[2–4] Further, catalytic aerobic oxidation of alcohols occurs *via* **1** and the bis(alkoxy) species.

Species **1** was generated by exposure of trans-Ru^{II}-(tmp)(MeCN)$_2$ (10 mg, 0.010 mmol) in benzene (10 ml) to air at about 20 °C;[1,5] the solution was then freeze-pumped several times, and Pr^{i}OH (10 µl, 0.13 mmol) was then added by vacuum transfer. Within 24 h, the bis(isopropoxy) species **3** was formed quantitatively according to the stoichiometry of eqn. (1). Complex **3** is isolated as a paramagnetic Ru^{IV} compound (μ_{eff} = 2.96 μ_B, S = 1), following extended

$$\text{Ru}^{VI}(\text{tmp})(\text{O})_2 \ \mathbf{1} + 3\text{Me}_2\text{CH(OH)} \rightarrow$$
$$\text{Ru}^{IV}(\text{tmp})(\text{OCHMe}_2)_2 \ \mathbf{3} + \text{Me}_2\text{CO} + 2\text{H}_2\text{O} \qquad (1)$$

evacuation of the product solution; a crystal was grown from a concentrated [^{2}H$_6$]benzene solution of **3** used for ^{1}H NMR spectra (see below). X-Ray analysis of a crystal of **3** reveals a structure with an inversion centre (Fig. 1),† and which is
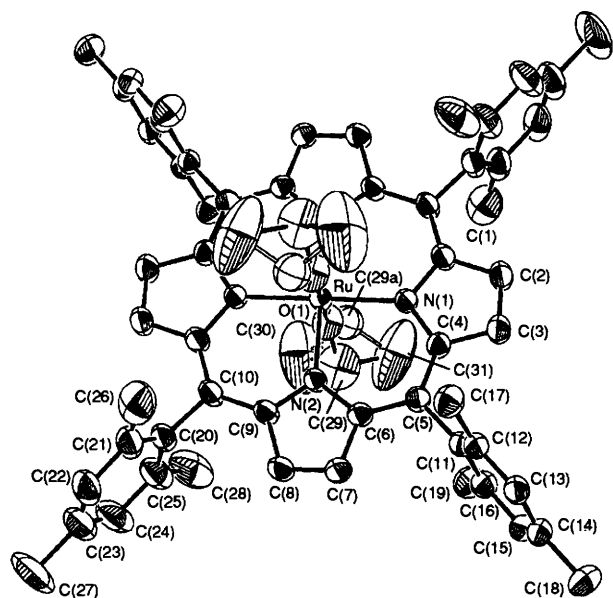

Fig. 1 The structure of **3** (H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Ru–O(1) 1.892(3), Ru–N(av.) 2.033, O(1)–C(29a) 1.18(3), O(1)–C(29) 1.34(1), C(29)–C(31) 1.55(2), C(29a)–C(31) 1.47(3), C(29)–C(30) 1.56(1), C(29a)–C(30) 1.66(3); Ru–O(1)–C(29) 139.7(5), Ru–O(1)–C(29a) 155(1), O(1)–C(29)–C(31) 103(1), O(1)–C(29)–C(30) 100(1), O(1)–C(29a)–C(30) 101(1), O(1)–C(29a)–C(31) 117(2). At the Ru, all cis-angles are 90 ± 1.2°.
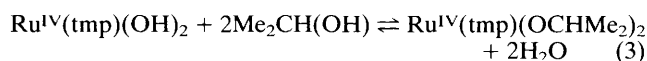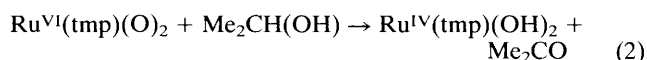
essentially octahedral at the Ru atom, with the metal in the porphyrin plane, and with axial isopropoxide ligands; the tetramesityl groups are perpendicular to the porphyrin plane, and the dimensions of the Ru(tmp) moiety are essentially the same as those found in the ruthenium(II) complex trans-Ru^{II}-(tmp)(MeCN)$_2$.[1] There are no significant non-bonding interactions involving the axial isopropoxides in which the central carbon atom is mirror-disordered about the plane defined by the O-atom and the two methyl C-atoms. The Ru–O distance of 1.892 Å is comparable to that found (1.944 Å) within the coordinated *p*-cresol of [Ru^{IV}(tpp)(*p*-OC$_6$H$_4$Me)]$_2$O, which is also a ruthenium(IV) complex but is diamagnetic with a linear Ru–O–Ru moiety (tpp = dianion of 5,10,15,20-tetraphenylporphyrin);[6] the averaged Ru–O bond length of the ethoxide/ethanol groups in the ruthenium(III) complex Ru^{III}(tpp)-(OEt)(EtOH) is longer at 2.019 Å.[6] The disorder problems limit discussion on the significance of the large Ru–O–C angles (139.7 and 155°), but nevertheless the angles are much larger than tetrahedral, implying considerable π-donation from the oxygen; the bonding situation seems similar to that discussed for Ru(porph)X$_2$ (X = Cl, Br) complexes, which have two unpaired electrons accommodated in a closely spaced t$_{2g}$ set (with either d$_{xy}$ or d$_{xz,yz}$ being lowest in energy).[7]

The ^{1}H NMR data for **3** [300 MHz, C$_6$D$_6$, 20 °C, δ (all singlets): −15.20 (12H, *Me*$_2$CH), −14.22 (2H, -C{H}O-), −11.95 (8, pyrrole-H), 2.85 (12H, *p*-Me), 2.90 (24H, *o*-Me), 7.52 (8H, *m*-H)] are entirely consistent with a Ru^{IV} paramagnetic species with D_{4h} symmetry;[1,2,7] the isotropic shifts of the porphyrin ligand within **3** generally conform to Curie behaviour from −60 to +60 °C, showing the existence of a single spin state over this temperature range. The previously reported ^{1}H NMR data for an *in situ* sample of **3** did not show the isopropoxide resonances because of broadening brought about by rapid exchange with the excess Pr^{i}OH present;[1] addition of this alcohol, MeOH, or EtOH to **3** demonstrates this exchange, all three systems showing similar spectra which have been previously assigned tentatively,[1] or definitively,[2] to Ru^{IV}(tmp)(OH)$_2$. The UV–VIS spectrum of **3** dissolved in benzene varies depending on the alcohol added because of the formation of different Ru^{IV}(tmp)(OR)$_2$ species [λ_{max}/nm (10^{-3}ε dm^3 mol^{-1} cm^{-1})]: R = Pr^i, 412(240), 522(29.0); R = Et, 408(230), 520(25.4), 658(3.8); R = Me, 406(200), 520(26.7).

We repeated the synthesis of Leung *et al.*[2] for the supposed **2** [from **1** formed *in situ* from Ru^{II}(tmp)(CO) and *m*-chloroperbenzoic acid] and isolated the bis(ethoxy) species which shows coordinated ethoxy in the ^{1}H NMR spectrum in C$_6$D$_6$: −12.90 (6H, CH$_3$), −7.48 (4H, CH$_2$); the reported data^2 in CD$_2$Cl$_2$–CD$_3$OD correspond to the species with coordinated OCD$_3$ and not to Ru^{IV}(tmp)(OH)$_2$. Similarly, the reported UV–VIS data in CH$_2$Cl$_2$–EtOH, with maxima at 408, 522 and 660 nm,[2] are those of the bis(ethoxy) species. Of note, this group mentioned some unpublished X-ray data for **2**, the structure being incompletely solved 'due to disorder of the two axial ligands and solvent molecules'; the reported Ru–O distance of 1.929(9) Å almost certainly refers to coordinated, disordered ethoxide. Within [Ru^{IV}(oep)(OH)]$_2$O (oep = dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin), the Ru–O(H) bond length is 2.195(26) Å.[8]

The stoichiometric oxidation of alcohols by higher-valent metal–oxo species has been well studied, especially for non-porphyrin ruthenium–oxo complexes;[9] mechanisms have

included as initial steps oxidative addition of the α-C–H bond of the alcohol to the Ru=O moiety to give an organoruthenium intermediate,[10] or transfer of the α-H as hydride to the oxo ligand.[11] The lack of readily available *cis*-sites in **1** tends to rule out oxidative addition pathways; reaction (2) involving stepwise H-atom transfers followed by reaction (3) readily accounts for the overall reaction of eqn. (1), but a process involving initial transfer of a hydrogen as hydride or proton cannot be ruled out.

$$Ru^{VI}(tmp)(O)_2 + Me_2CH(OH) \rightarrow Ru^{IV}(tmp)(OH)_2 + Me_2CO \quad (2)$$

$$Ru^{IV}(tmp)(OH)_2 + 2Me_2CH(OH) \rightleftharpoons Ru^{IV}(tmp)(OCHMe_2)_2 + 2H_2O \quad (3)$$

Of particular interest, in the presence of air, benzene solutions of **1** or **3** (*ca.* 1 mmol dm^{-3}) effect catalytic oxidation of Pr^{i}OH (*ca.* 10 mmol dm^{-3}) to Me$_2$CO; turnovers of about 1.5/day are realized at ambient conditions. Alcohol oxidations catalysed by non-porphyrin ruthenium–oxo species require O-atom donors or electrochemical methods for regeneration of the oxo ligand,[9,11] including some *trans*-dioxoruthenium(vi) species containing macrocyclic, N-donor tetraaza ligands, although these effect aerobic oxidation (marginally catalytic) of benzyl alcohol to benzaldehyde at ambient conditions.[12] Likewise, **1** also catalytically oxidizes benzyl alcohol to benzaldehyde, with turnovers similar to the isopropanol oxidation. The bis(alkoxy) species **3**, when exposed to air (but *not* dry O$_2$) regenerates the dioxo species **1**, and this reaction, which probably proceeds *via* an initial step that is the reverse of eqn. (3), coupled with reaction (1), accounts for the overall catalytic process. Further studies on the catalytic process and its mechanism, particularly with the more robust tetra(2,6-dichlorophenyl)porphyrin systems,[4] are in progress.

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Footnote

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