Oxo-ruthenium(v) Complexes of Macrocyclic Tetradentate Tertiary Amines that Function as Active Electrochemical Oxidative Catalysts, and *X*-Ray Crystal Structure of *trans*-[Ru$^{\text{IV}}$(tmc)O(Cl)]ClO$_4$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)

Chi-Ming Che,*[a] Kwok-Yin Wong,[a] and Thomas C. W. Mak*[b]

[a] *Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong*
[b] *Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong*

Ruthenium(v) mono-oxo complexes electrochemically generated from *trans*-[Ru$^{\text{IV}}$LO(Cl)]$^+$ (L = tmc or 15-tmc; tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane, 15-tmc = 1,4,8,12-tetramethyl-1,4,8,12-tetra-azacyclopentadecane) are active oxidative catalysts for the conversion of alcohol into aldehyde; *X*-ray analysis of *trans*-[Ru$^{\text{IV}}$(tmc)O(Cl)]ClO$_4$ yielded Ru=O 1.765(7) Å and Ru–Cl 2.505(3) Å.

The perferryl complex (FeO^{3+}) has long been speculated to play an important role in the enzymatic oxidative reactions of cytochrome P-450.[1,2] However, its existence is still controversial, and the analogous and presumably more stable mono-oxo complexes of Ru$^{\text{V}}$ and Os$^{\text{V}}$ have never been reported. Recent studies have shown that the tetradentate macrocyclic tertiary amines, tmc and 15-tmc (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane: 15-tmc = 1,4,8,12-tetramethyl-1,4,8,12-tetra-azacylopentadecane), by virtue of their strong σ-donor properties, are capable of stabilizing metal-oxo complexes in unusually high oxidation states.[3—5] We describe here the first example of electrochemical generation of a $[Ru^{V}{=}O]^{3+}$ complex; preliminary results indicate that this species is an extremely active catalyst for the oxidation of alcohol.

Treatment of an acetone suspension of *trans*-$[Ru^{VI}(tmc)O_2](ClO_4)_2$ with an excess of PPh_3 resulted in the formation of a deep-yellow clear solution. Upon subsequent addition of diethyl ether, a yellow solid was obtained in high yield (>80%). Recrystallization of this solid in acetone–diethyl ether gave *trans*-$[Ru^{IV}(tmc)O(Cl)]ClO_4$ (**1**).[†] *trans*-$[Ru^{IV}(15\text{-}tmc)O(Cl)]ClO_4$ (**2**) was similarly prepared.[†] As expected for a d^4 mono-oxo complex with triplet ground state $[(d_{xy})^2(d_{xz})^1(d_{yz})^1]$, (**1**) and (**2**) are paramagnetic with $\mu_{eff.}$ *ca.* 2.8 μ_B. The u.v.–visible spectra and cyclic voltammograms of (**1**) and (**2**) in water are identical with those of the corresponding *trans*-$[Ru^{IV}(tmc)O(H_2O)]^{2+}$ and *trans*-$[Ru^{IV}(15\text{-}tmc)O(H_2O)]^{2+}$ species,[4] indicating that the co-ordinated chloride is extremely substitutionally labile. Consistent with these results, (**1**) or (**2**) behaves as a 1:2 electrolyte in H_2O (Λ_M = 243 ohm^{-1} mol^{-1} cm^2). Complex (**1**), originally thought to be *trans*-$[Ru^{IV}(tmc)O(H_2O)](ClO_4)_2$ has also been characterized by *X*-ray crystallography.

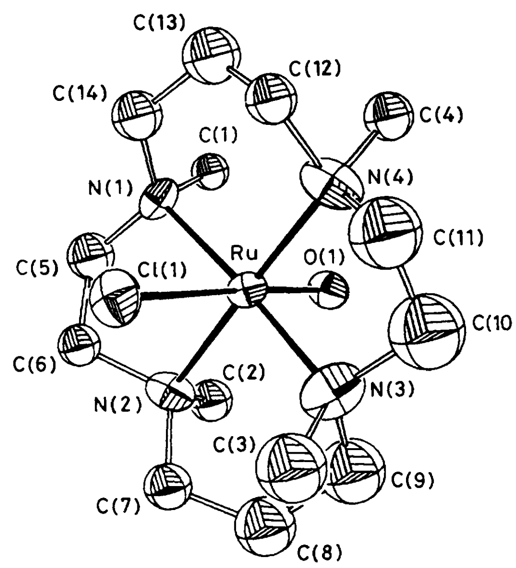

Figure 1. A perspective view of the $[Ru^{IV}(tmc)O(Cl)]^+$ cation in (**1**) with atom labelling. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å), bond angles (°), and torsion angles (°): Ru–O(1), 1.765(7); Ru–Cl(1), 2.505(3); Ru–N(1), 2.16(2); Ru–N(2), 2.16(1); Ru–N(3), 2.09(2); Ru–N(4), 2.07(2); O(1)–Ru–N(1), 92.7(8); O(1)–Ru–N(2), 90.2(9); O(1)–Ru–N(3), 91.7(9); O(1)–Ru–N(4), 88.7(9); O(1)–Ru–Cl(1), 177.2(4); N(1)–Ru–N(2), 84.1(6); N(2)–Ru–N(3), 94.7(7); N(3)–Ru–N(4), 84.3(8); N(4)–Ru–N(1), 96.9(8); N(1)–C(5)–C(6)–N(2), −51(2); C(5)–C(6)–N(2)–C(7), 174(2); C(6)–N(2)–C(7)–C(8), −172(2); N(2)–C(7)–C(8)–C(9), 37(3); C(7)–C(8)–C(9)–N(3), 37(3); C(8)–C(9)–N(3)–C(10), 172(2); C(9)–N(3)–C(10)–C(11), 166(2); N(3)–C(10)–C(11)–N(4), −65(3); C(10)–C(11)–N(4)–C(12), 167(3); C(11)–N(4)–C(12)–C(13), −174(2); N(4)–C(12)–C(13)–C(14), 66(2); C(12)–C(13)–C(14)–N(1), −67(3); C(1)–N(1)–C(5)–C(6), 132(2); C(5)–C(6)–N(2)–C(2), −64(2); C(3)–N(3)–C(10)–C(11), −89(3); C(10)–C(11)–N(4)–C(4), −90(3).

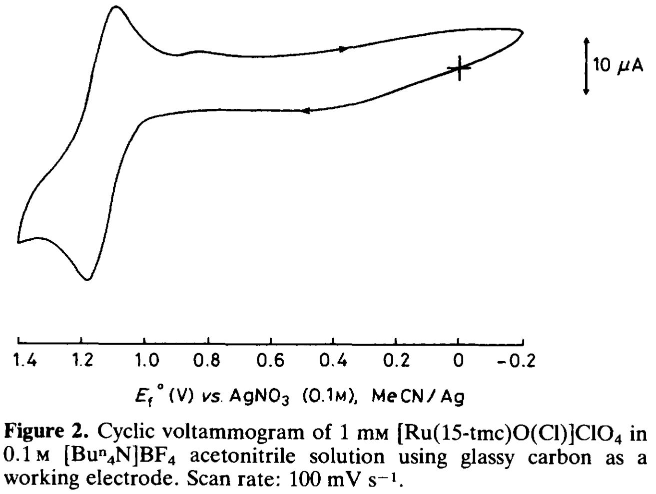

Figure 2. Cyclic voltammogram of 1 mM $[Ru(15\text{-}tmc)O(Cl)]ClO_4$ in 0.1 M $[Bu^n{}_4N]BF_4$ acetonitrile solution using glassy carbon as a working electrode. Scan rate: 100 mV s^{-1}.

trans-$[Ru^{IV}LO(Cl)]ClO_4$
(**1**) L = tmc
(**2**) L = 15-tmc

Crystal Data: $C_{14}H_{32}N_4O_5Cl_2Ru$ (**1**), yellow–brown flat prisms, *M* = 508.40. Orthorhombic, space group $Pna2_1$ (from intensity statistics and confirmed by structure determination), *a* = 12.254(4), *b* = 15.470(4), *c* = 10.821(2) Å, *U* = 2051(1) Å^3, D_m (flotation in CCl_4–$BrCH_2CH_2Br$) = 1.63 g cm^{-3}, *Z* = 4, D_c = 1.646 g cm^{-3}, *F*(000) = 1047.84, μ(Mo-K_α) = 10.43 cm^{-1}. Dimensions of single crystal sealed in 0.5 mm Lindemann glass capillary: 0.28 × 0.24 × 0.06 mm, mean μr = 0.08, transmission factors 0.716 to 0.909.

Intensities (*h, k, l*; $2\theta_{max.}$ = 54°; 2349 unique and 1697 observed reflections) were recorded at 22 °C using monochromatized Mo-K_α radiation (λ = 0.71069 Å). Structure solution was accomplished by Patterson and Fourier methods. The O atoms of the perchlorate group were found to be badly

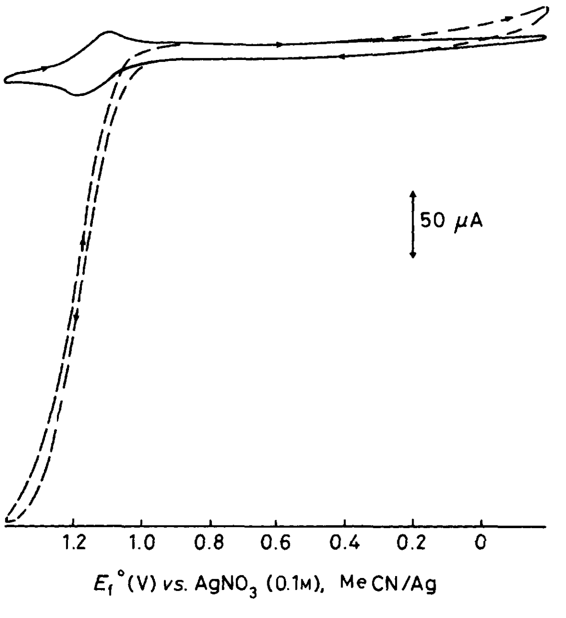

Figure 3. Cyclic voltammogram of 1 mM $[Ru(tmc)O(Cl)]ClO_4$ in 0.1 M $[Bu^n{}_4N]BF_4$ acetonitrile solution showing the catalytic current upon addition of benzyl alcohol: —— absence of benzyl alcohol; - - - 1% v/v benzyl alcohol added. Scan rate: 100 mV s^{-1}.

[†] The origin of the co-ordinated chloride ligand in (**1**) and (**2**) is uncertain; presumably this resulted from the reduction of ClO_4^- by PPh_3. Satisfactory elemental analysis results have been obtained for both (**1**) and (**2**). The 15-tmc ligand was synthesized by essentially the same procedure as described for 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane in ref. 6.

disordered and therefore treated as eight fractional atoms with variable site occupancy factors and isotropic temperature factors. Refinement proceeded with isotropic thermal parameters for the C atoms and anisotropic ones for the remaining non-hydrogen atoms in the asymmetric unit. The methylene H atoms were generated geometrically (C–H = 0.96 Å) and included in structure factor calculations with fixed isotropic thermal parameters. The N–C(methyl), N–C(methylene), and C–C bond distances were treated as free variables and refined to the values 1.57(1), 1.52(1), and 1.49(1) Å, respectively. The site occupancies of the disordered perchlorate O atoms ranged from 0.22(4) to 1.00(6), adding up to 4.18 which compares well with the expected value of 4. Convergence for 171 variables was reached at $R_F = 0.077$ and $R_w = 0.096$ with weighting scheme $w = [\sigma^2(|F_o|) + 0.0018|F_o|^2]^{-1}$. Details of data collection and computation are as described in the preceding paper (ref. 7).[‡]

A perspective view of the *trans*-$[\mathrm{Ru^{IV}(tmc)O(Cl)}]^+$ cation in complex (**1**) is illustrated in Figure 1. The macrocyclic ligand adopts a 'three up, one down', [§] or (*R,S,R,R*), set of nitrogen configurations with three *N*-methyl groups *cis* to the Ru=O bond, in contrast to the 'all four down", namely (*R,S,R,S*), configuration found in *trans*-$[\mathrm{Ru^{IV}(tmc)O(MeCN)}](\mathrm{PF_6})_2$ (**3**).[3] Accordingly the two six-membered chelate rings have different conformations, namely twist-boat [involving co-ordination of N(2) and N(3) to the metal] and chair, and the five-membered chelate rings are both *gauche*. The measured Ru=O bond length of 1.765(7) Å closely matches the corresponding value of 1.755(5) Å in (**3**), as do the Ru–N distances in these two related complexes. The Ru–Cl bond length of 2.505(3) Å is *ca.* 0.16 Å longer than those found in *cis*- and *trans*-$[\mathrm{Ru(cyclam)Cl_2}]^+$ (cyclam = 1,4,8,11-tetra-azacyclotetradecane),[8,9] thereby providing a rationale to the observed substitutional lability of the co-ordinated chloride in (**1**).

Both (**1**) and (**2**) behave as 1 : 1 electrolytes in acetonitrile (Λ_M = 120 ohm^{-1} mol^{-1} cm^2) and exhibit a quasi-reversible one-electron oxidation couple at $E_f^\circ = 1.1$ V (ΔE_p *ca.* 80 mV) *vs.* $\mathrm{cp_2Fe^+/cp_2Fe^0}$ couple (Figure 2).[¶] The σ-saturated nature of the ligands in (**1**) or (**2**) indicates that the oxidation process is essentially metal-centred, and we therefore attribute this couple to the electrode reaction shown in equation (1).

$$trans\text{-}[\mathrm{Ru^{IV}(tmc)O(Cl)}]^+ - e^- \rightarrow trans\text{-}[\mathrm{Ru^{V}(tmc)O(Cl)}]^{2+} \qquad (1)$$

No $\mathrm{Ru^V{=}O/Ru^{IV}{=}O}$ couple has been observed in the case of *trans*-$[\mathrm{Ru^{IV}(tmc)O(MeCN)}]^{2+}$, and this is understandable in view of its higher charge over (**1**) or (**2**). Importantly, the electrochemically generated *trans*-$[\mathrm{Ru^{V}LO(Cl)}]^{2+}$ (L = tmc or 15-tmc) species is an active oxidative catalyst. The cyclic voltammogram of (**1**) in acetonitrile containing 1% benzyl alcohol (Figure 3) revealed the presence of a large catalytic current at E_f° *ca.* 1.3 V (*vs.* the $\mathrm{cp_2Fe^+/cp_2Fe^0}$ couple), indicating that the *trans*-$[\mathrm{Ru^{V}(tmc)O(Cl)}]^{2+}$ species, once generated, rapidly oxidized the alcohol. Controlled-potential electrolysis experiments showed that benzaldehyde (identified by gas chromatography) was produced. This reaction was catalytic as over fifty turnovers of benzyl alcohol/catalyst were found. Under the same conditions, however, the $\mathrm{Ru^{IV}{=}O}$ species of tmc or 15-tmc exhibited no activity towards the oxidation of alcohol.

Received, 18th March 1985; Com. 359

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[†] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[§] The terminology of ref. 6 is used with an *N*-methyl group *cis* to the Ru=O bond arbitrarily designated as 'up'.

[¶] Under these conditions, the E_f° value and the peak-to-peak separation of the $\mathrm{cp_2Fe^+/cp_2Fe^0}$ couple are 0.045 V *vs.* $\mathrm{AgNO_3}$ (0.1 M in acetonitrile)/Ag and 80 mV, respectively.