

## Metal-Oxo Photo-oxidants: Photochemical Oxidation of Hydrocarbons by *trans*-Dioxo complexes of Ruthenium(vI) and Osmium(vI)

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The synthesis of *trans*-[Ru<sup>VI</sup>(L)(O)<sub>2</sub>]Y<sub>2</sub> (Y = PF<sub>6</sub> or ClO<sub>4</sub>) and *trans*-[Ru<sup>IV</sup>(L)(NCO)(O)]ClO<sub>4</sub> {L = *meso*-1,2,6,10,11-pentamethyl-2,6,10-triaza[11](2,6)pyridinophane} is described; irradiation of *trans*-[Ru<sup>VI</sup>(L)(O)<sub>2</sub>]<sup>2+</sup> and [Os<sup>VI</sup>(CN)<sub>4</sub>(O)<sub>2</sub>]<sup>2-</sup> ( $\lambda > 330$  nm) in presence of organic substrates yielded the corresponding oxidized organic products indicating that the (d<sub>xy</sub>)<sup>1</sup>(d<sub>π</sub>)<sup>\*</sup> excited states of Ru<sup>VI</sup>- and Os<sup>VI</sup>-oxo complexes are reactive towards epoxidation of alkenes and to oxidation of C-H bonds.

Recently there has been much interest in the photochemical oxidation of hydrocarbons by transition metal complexes.<sup>1-5</sup> Spectroscopic studies of *trans*-dioxorhenium(v) complexes<sup>1</sup> suggested the possibility of developing powerful metal-oxo photo-oxidants through light excitation of metal-oxo complexes.<sup>1,5,6</sup> In support of this hypothesis, we describe here results illustrating the reactivity of excited states of ruthenium(vI) and osmium(vI) oxo complexes in epoxidation of alkenes and oxidation of C-H bonds.

The preparation and u.v.-visible spectral data of ruthenium complexes with the ligand L<sup>7</sup> are summarized in Scheme 1. The structures of *trans*-[Ru<sup>III</sup>(L)Cl<sub>2</sub>]ClO<sub>4</sub> and *trans*-[Ru<sup>IV</sup>(L)(NCO)(O)]ClO<sub>4</sub> have been established by X-ray crystallography.<sup>8</sup> *trans*-[Ru<sup>VI</sup>(L)(O)<sub>2</sub>]Y<sub>2</sub> (Y = PF<sub>6</sub> or ClO<sub>4</sub>) complexes were isolated as diamagnetic yellow solids with  $\nu_{as}$  (Ru=O) 850 cm<sup>-1</sup>. These complexes are more powerful

oxidants than *trans*-[Ru<sup>VI</sup>(tmc)O<sub>2</sub>]<sup>2+</sup> (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) [ $E_1$ (Ru<sup>VI</sup>/Ru<sup>IV</sup>) 0.76 V vs. standard calomel electrode (S.C.E.) at pH 1.1]<sup>†</sup> and more stable to light.<sup>‡</sup> The electronic spectra of *trans*-

<sup>†</sup> Satisfactory elemental analyses have been obtained for *trans*-[Ru<sup>VI</sup>(L)(O)<sub>2</sub>][ClO<sub>4</sub>]<sub>2</sub>. The electrochemistry of *trans*-[Ru<sup>VI</sup>(L)(O)<sub>2</sub>]<sup>2+</sup> is very similar to that of *trans*-[Ru<sup>VI</sup>(tmc)(O)<sub>2</sub>]<sup>2+</sup> (ref. 6a); the  $E_1$  value refers to the electrode reaction, *trans*-[Ru<sup>VI</sup>(L)(O)<sub>2</sub>]<sup>2+</sup> + 2H<sup>+</sup> + 2e<sup>-</sup> → *trans*-[Ru<sup>IV</sup>(L)(O)(OH<sub>2</sub>)]<sup>2+</sup> at pH 1.1.

<sup>‡</sup> The photochemical reactions were carried out with a high pressure 350 W short arc mercury lamp equipped with filters. Irradiation of *trans*-[Ru<sup>VI</sup>(L)(O)<sub>2</sub>]<sup>2+</sup> in 0.1 M-CF<sub>3</sub>CO<sub>2</sub>H at 350-450 nm for 1.5 h resulted in no optical spectral changes of the solution. However, *trans*-[Ru<sup>VI</sup>(tmc)(O)<sub>2</sub>]<sup>2+</sup> rapidly decomposed (within minutes) upon photolysis ( $\lambda > 350$  nm) in aqueous solution.

**Table 1.** Photo-oxidation of organic substrates by *trans*-[Ru<sup>VI</sup>(L)(O)<sub>2</sub>][ClO<sub>4</sub>]<sub>2</sub> in acetonitrile<sup>a</sup> (3 ml) at 25 °C.

Substrate	Product <sup>b</sup>	Yield <sup>c</sup> /%	[Ru <sup>VI</sup> (L)(O) <sub>2</sub> ]- [ClO <sub>4</sub> ] <sub>2</sub> employed/mg	Irradiation time/h
Norbornene (150 mg)	<i>exo</i> -2,3-Epoxy-norbornane	44	50	1.5
Cyclohexene (1 ml)	Cyclohexen-2-one	50	47	1.5
	Cyclohexen-2-ol	25		
<i>trans</i> -Stilbene (200 mg)	<i>trans</i> -Stilbene oxide	8	40	3.5
Dibenzyl sulphide (32 mg)	Dibenzyl sulphoxide	34	20	4.0
Propan-2-ol (2 ml)	Acetone	79	32	3.0

<sup>a</sup> The acetonitrile solutions were degassed with argon for 15 min before irradiation. <sup>b</sup> The products were identified by g.c.-mass spectrometry, except for *trans*-stilbene oxide and dibenzyl sulphoxide which were identified by <sup>1</sup>H n.m.r. spectroscopy (90 MHz). <sup>c</sup> Based on the amount of Ru<sup>VI</sup> complex used.

**Table 2.** Photo-oxidation of organic substrates by [Ph<sub>4</sub>As]<sub>2</sub>[Os<sup>VI</sup>(CN)<sub>4</sub>(O)<sub>2</sub>] (30–40 mg) in acetonitrile<sup>a</sup> (3 ml) at 25 °C (irradiation time, 4.5 h).

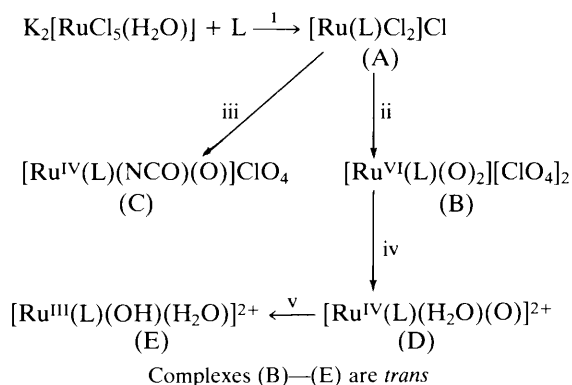
Substrate	Product <sup>b</sup>	Yield <sup>c</sup> /%
Benzyl alcohol (0.2 ml)	Benzaldehyde	84
Toluene (0.2 ml)	Benzaldehyde	21
Cyclohexene (0.2 ml)	Cyclohexenone	35
	Cyclohexen-2-ol	63
	Cyclohexene epoxide	9
Styrene (0.2 ml)	Styrene oxide	62
	Benzaldehyde	12
<i>trans</i> -Stilbene (50 mg)	<i>trans</i> -Stilbene epoxide	0
	Benzaldehyde	12
<i>p</i> -Methylbenzyl alcohol (50 mg)	<i>p</i> -Tolualdehyde	176
Norbornene (50 mg)	<i>exo</i> -2,3-Epoxy-norbornane	40
Cyclohexane (0.2 ml)	Cyclohexanone	25
	Cyclohexanol	10

<sup>a</sup> The acetonitrile solutions were degassed with argon for 15 min before irradiation. <sup>b</sup> Except *trans*-stilbene epoxide, all organic products were identified by g.c.-mass spectrometry. <sup>c</sup> Based on amount of Os<sup>VI</sup> complex used.

[Ru<sup>VI</sup>(L)(O)<sub>2</sub>]<sup>2+</sup> and the previously prepared osmium complex<sup>5b</sup> [Ph<sub>4</sub>As]<sub>2</sub>[Os<sup>VI</sup>(CN)<sub>4</sub>(O)<sub>2</sub>] in MeCN display vibronic structured absorption bands (Ru<sup>VI</sup> 400, Os<sup>VI</sup><sup>5b</sup> 320 and 370 nm) corresponding to a (d<sub>xy</sub>)<sup>2</sup> → (d<sub>xy</sub>)<sup>1</sup>(d<sub>π\*</sub>)<sup>1</sup> (d<sub>π\*</sub> = d<sub>xz</sub>, d<sub>yz</sub>) transition.<sup>1,5,6</sup> While the Ru<sup>VI</sup> complex is non-emissive in solution, the (d<sub>xy</sub>)<sup>1</sup>(d<sub>π\*</sub>)<sup>1</sup> triplet of Os<sup>VI</sup> is a powerful oxidant with a lifetime of 0.4 μs in MeCN at 25 °C.<sup>5b</sup>

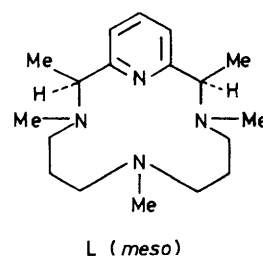
At room temperature, irradiation (>350 nm)<sup>‡</sup> of *trans*-[Ru<sup>VI</sup>(L)(O)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> {or [Ph<sub>4</sub>As]<sub>2</sub>[Os<sup>VI</sup>(CN)<sub>4</sub>(O)<sub>2</sub>], >330 nm} with organic substrates in degassed MeCN yielded the corresponding oxidized products, identified by g.c.-mass spectrometry and <sup>1</sup>H n.m.r. spectroscopy (Tables 1 and 2). Under similar conditions thermal reactions were negligible.§ At 10 °C, photo-epoxidation of norbornene by these metal-oxo complexes to give norbornene oxide also occurred (40–50% yield) after 3–4 h irradiation. After all the photoreactions, the electronic spectrum of the ruthenium product (λ<sub>max</sub> ~ 340 nm) closely matched that of *trans*-[Ru<sup>II</sup>(L)(MeCN)<sub>2</sub>]<sup>2+</sup>. Assuming this is the photo-product, the

‡ Slow thermal oxidation of propan-2-ol and cyclohexene by *trans*-[Ru<sup>VI</sup>(L)(O)<sub>2</sub>][ClO<sub>4</sub>]<sub>2</sub> has been observed. Reactions of *trans*-[Ru<sup>VI</sup>(L)(O)<sub>2</sub>][ClO<sub>4</sub>]<sub>2</sub> with norbornene and stilbene at 50 °C for 20 h yielded no *exo*-2,3-epoxy-norbornane nor *trans*-stilbene oxide, respectively. [Ph<sub>4</sub>As]<sub>2</sub>[Os<sup>VI</sup>(CN)<sub>4</sub>(O)<sub>2</sub>] has been found to be inert towards oxidation of alcohols and cyclohexene and epoxidation of alkenes.



**Scheme 1.** Reagents and conditions: i, EtOH, reflux, 24 h; ii, excess of AgSO<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Me-*p*, H<sub>2</sub>O, ~70 °C, then 30% H<sub>2</sub>O<sub>2</sub>; iii, as for ii, but with H<sub>2</sub>O<sub>2</sub> + NaNCO; iv, reduction at 0.60 V vs. S.C.E.; v, reduction at 0.25 V vs. S.C.E.

Electronic spectra, in 0.1 M CF<sub>3</sub>CO<sub>2</sub>H, except for (C) in MeCN = λ<sub>max</sub>/nm (ε) (A), 385 (3170) and 320 (2060); (B) 402 (630), 320 (2560), and 265 (7900); (C) 302 (5170) and 268 (4130); (D) 292 (2310), 261 (3970), and 230 (4380); (E), 335 (3020) and 242 (6310).



molar ratios of Ru<sup>II</sup> product to the starting compound *trans*-[Ru<sup>VI</sup>(L)(O)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> are 0.44, 0.28, and 0.41 for the photoreactions with propan-2-ol, norbornene, and cyclohexene, respectively. In each of its photoreactions, [Ph<sub>4</sub>As]<sub>2</sub>[Os<sup>VI</sup>(CN)<sub>4</sub>(O)<sub>2</sub>] was transformed to a species having no significant absorption at wavelengths greater than 320 nm. As *trans*-[Ru<sup>IV</sup>(L)(NCO)(O)]<sup>+</sup> was found to be inert both thermally and photochemically, to the organic substrates it is unlikely that the Ru–L–oxo complex is the active intermediate in the photoreactions of *trans*-[Ru<sup>VI</sup>(L)(O)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>.

Excitation of *trans*-[Ru<sup>VI</sup>(L)(O)<sub>2</sub>]<sup>2+</sup> or [Os<sup>VI</sup>(CN)<sub>4</sub>(O)<sub>2</sub>]<sup>2-</sup> in the 300–400 nm region produces the (d<sub>xy</sub>)<sup>1</sup>(d<sub>π\*</sub>)<sup>1</sup> excited state which has a weaker M–O band than when in the ground state and hence is a better oxo-transfer reagent [ν<sub>Ru–O</sub>: <sup>1</sup>A<sub>1g</sub>

850,  ${}^3E_g$  600—650  $\text{cm}^{-1}$ ;  $\nu_{\text{Os=O}}$ :  ${}^1A_{1g}$  ~870,  ${}^3E_g$  700  $\text{cm}^{-1}$ ].<sup>5b¶</sup> Experimentally, photochemical, but not thermal, epoxidation of alkenes by these metal complexes was observed§ as would be predicted. The excited state of  $[\text{Os}^{\text{VI}}(\text{CN})_4(\text{O})_2]^{2-}$ , is even capable of oxidizing unactivated C—H bonds in cyclohexane, illustrating the potential uses of  $d^2$ -*trans*-dioxo metal complexes of Ru and Os in photo-oxidation of hydrocarbons.

We acknowledge financial support from the University of Hong Kong and the Croucher Foundation. V. W.-W. Y is a Croucher Foundation Studentship and Li Po Chun Scholarship holder.

Received, 16th July 1987; Com. 1036

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¶ The M—O stretching frequencies in the excited states were estimated from the vibrational spacing in the  $(d_{xy})^2 \rightarrow (d_{xy})^1(d_{\pi^*})^1$  transition. See also refs. 1 and 5b.

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