Electronic Supplementary Information

Mechanistic insight into the reactions of hydride transfer *versus* hydrogen atom transfer by a *trans*-dioxoruthenium(VI) complex

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Electronic Supplementary Information, ESI 1

X-ray crystallography

Single crystals of 1 were obtained by slow diffusion of diethyl ether into the CH₃CN solution of 1. The crystals of 1 suitable for X-ray studies were picked up and mounted on a Bruker SMART AXS diffractometer equipped with a monochromator (Mo $K_{\alpha} = 0.71073$ Å). The CCD data were integrated and scaled using Bruker-SAINT software package while SHEXTL V 6.12 was used for solving and refining the structure.^{S1} Non-hydrogen atoms were refined with anisotropic displacement parameters. However, H atoms could not be geometrically positioned due to the relatively high degree of disorders. The crystallographic data for 1 was listed in Table S1. CCDC-1049483 for 1 contains the supplementary crystallographic data for this paper. These data be obtained free of charge can via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or 12, deposit@ccdc.cam.ac.uk).

References

S1. G. M. Sheldrick, SHELXTL/PC. Version 6.12 for Windows XP, Bruker AXS Inc., Madison, WI, USA, 2001.

Empirical formula	C14Cl2N4O10Ru
Formula weight (g mol ⁻¹)	556.15
Temperature (K)	170(2)
Wavelength (Å)	0.71073
Crystal system/space group	Monoclinic, <i>P</i> 2 _{1/c}
Unit cell dimensions	
<i>a</i> (Å)	6.3282(6)
b (Å)	16.9820(17)
<i>c</i> (Å)	10.1870(10)
α (°)	90.00
β (°)	94.132(2)
γ (°)	90.00
Volume (Å ³)	1091.91(18)
Ζ	2
Calculated density (g/cm ⁻³)	1.692
Absorption coefficient (mm ⁻¹)	1.018
<i>F</i> (000)	540
Crystal size (mm ³)	0.4 imes 0.2 imes 0.1
Theta range for data collection (°)	2.34 to 27.42
Reflections collected	6032
Independent reflections $[R_{(int)}]$	2150 (0.0320)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1679 / 0 / 179
Goodness-of-fit on F^2	1.100
Final <i>R</i> indices $[I>2\sigma(I)]$	$R_1 = 0.0547, wR_2 = 0.1534$
R indices (all data)	$R_1 = 0.0650, wR_2 = 0.1574$
Extinction coefficient	0.0041(16)
Largest diff. peak and hole $(e/Å^3)$	1.554 and -0.527

Table S1 Crystal data and structure refinement for *trans*-[Ru^{VI}(TMC)(O)₂](ClO₄)₂ (1).

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Fig. S1 ORTEP diagram of $[Ru^{VI}(TMC)(O)_2]^{2+}$ unit in **1** showing the atom numbering scheme and 30 % probability ellipsoids [Symmetry code: (i) 1-x, 1-y, 1-z]. Selected bond distances (Å): Ru-O1 1.712(4), Ru-N1 2.149(4), Ru-N2 2.146(4). H atoms could not be geometrically positioned due to the relatively high degree of disorders.



Fig. S2 ESI-MS spectrum of the reaction solution obtained in the reaction of **1** (1.0 mM) with AcrH₂ (20 mM) in CH₃CN at 0 °C. The peaks at m/z = 194.1, 207.5, 473.0 and 514.0 correspond to AcrH⁺ (*calc.* m/z = 194.1), [Ru^{IV}(TMC)(O)(CH₃CN)]²⁺ (*calc.* m/z = 207.6), [Ru^{IV}(TMC)(O)(ClO₄)]⁺ (*calc.* m/z = 473.1) and [Ru^{IV}(TMC)(O)(ClO₄)(CH₃CN)]⁺ (*calc.* m/z = 514.1), respectively.



Fig. S3 Plots of first-order rate constant (k_{obs}) against the concentration of NADH analogues to determine the second-order rate constants (k_{HT}) in the oxidation of (a) AcrH₂, (b) AcrD₂, (c) AcrHMe and (d) AcrHEt by 1 in CH₃CN at 0 °C.



Fig. S4 Plot of log $k_{\rm HT}$ for hydride transfer from NADH analogues to 1 in CH₃CN at 0 °C *versus* log $k_{\rm d}$ for deprotonation of AcrHR⁺⁺ (R = H, Me and Et) in CH₃CN at 25 °C. The rate constants of deprotonation ($k_{\rm d}$) of AcrHR⁺⁺ were taken from ref 21 in Text.



Fig. S5 (a) Cyclic voltammograms of 1 (1.0 mM) and the complete reaction solution obtained in the reaction of 1 (1.0 mM) and DHA (50 mM) in deaerated CH₃CN containing 0.10 M TBAPF₆ at 25 °C. (b) Cyclic voltammogram of $[Ru^{IV}(TMC)(O)(CH_3CN)](ClO_4)_2$, which is an authentic reference, in deaerated CH₃CN containing 0.10 M TBAPF₆ at 25 °C. A Pt working electrode was used with a scan rate of 100 mV s⁻¹.



Fig. S6 Plots of first-order rate constant (k_{obs}) against the concentration of alkyl hydrocarbons to determine the second-order rate constants (k_{HAT}) in the oxidation of (a) xanthene, (b) xanthene- d_2 , (c) DHA and (d) CHD by **1** in CH₃CN at 35 °C.