

Photocatalytic and aerobic oxidation of saturated alkanes by a neutral luminescent *trans*-dioxoosmium(vi) complex [OsO₂(CN)₂(dpphen)]

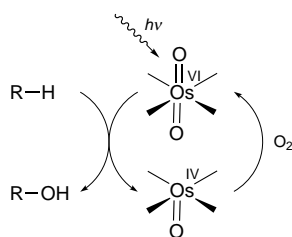
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A neutral *trans*-dioxoosmium(vi) complex [OsO₂(CN)₂(dpphen)] (dpphen = 4,7-diphenyl-1,10-phenanthroline) is prepared and characterized by X-ray crystal analysis; the excited state is long-lived, emissive and oxidizing [$E^\circ(\text{Os}^{\text{VI}-\text{V}}) = 2.15 \text{ V vs. NHE}$; lifetime = 0.95 μs ; quantum yield = 5×10^{-4} ; $\lambda_{\text{em}}(\text{max.}) = 650 \text{ nm}$]; under UV-VIS irradiation and in the presence of dioxygen, cyclohexane is oxidized to cyclohexanol and cyclohexanone with a turnover number of 16; secondary C-H bonds of propane and primary C-H bonds of *n*-hexane are also oxidized.

The search for new metal catalysts for aerobic oxidation of saturated alkanes has continued to receive general interest.¹ One approach to this area is to develop highly oxidizing metal-oxo complexes through irradiation with UV light as represented in Scheme 1.^{2,3}



Scheme 1

Previous studies revealed that *trans*-[Os^{VI}(tmc)O₂]²⁺ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) is capable of oxidizing a wide variety of organic substrates in acetonitrile upon UV-VIS irradiation.^{2,4} However, the photo-reduced product *trans*-[Os^{IV}(tmc)(MeCN)₂]²⁺ is stable with regard to aerobic oxidation back to the starting [Os^{VI}(tmc)O₂]²⁺.⁵ Herein is described a neutral *trans*-dioxoosmium(vi) complex [OsO₂(CN)₂(dpphen)] **1** (dpphen = 4,7-diphenyl-1,10-phenanthroline) which can mediate photocatalytic oxidation of saturated alkanes in the presence of dioxygen.

Addition of dpphen in CH₂Cl₂ to a freshly prepared aqueous solution of K₂[OsO₂(OH)₂(CN)₂]⁶ and in the presence of NBu₄Cl at room temp. gave complex **1** in 85% yield.† A perspective view of the molecule is shown in Fig. 1.‡ Similarly to most octahedral *trans*-dioxoosmium(vi) complexes,^{2d} the OsO₂ moiety is close to linear with the average Os-O distance and O=Os=O angle being 1.722(6) Å and 172.6(2)°, respectively.

Complex **1** is soluble in acetonitrile, dichloromethane and benzene. In MeCN, it shows an intense high energy absorption at $\lambda = 290 \text{ nm}$ ($\epsilon = 35\,840 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and a shoulder at 360 (970). Compared with *trans*-[Os^{VI}(tmc)O₂]²⁺, it has a much higher absorptivity in the UV region and this is attributed to the mixing of intraligand $\pi-\pi^*$ and spin-allowed $p_\pi(\text{O}^{2-})-d_{\pi^*}(\text{Os}^{\text{VI}})$ charge-transfer transitions.⁷ In this regard, dpphen serves as an antenna for UV light. As with other *trans*-dioxoosmium(vi) complexes,² **1** is emissive in the solid state

and in solution at room temp. Emission occurs at 635 nm with an excited state lifetime of 0.95 μs in MeCN. The E_{0-0} value, estimated from the 77 K solid-state emission spectrum is 2.11 eV and the $E^\circ(\text{Os}^{\text{VI}-\text{V}})$ by cyclic voltammetry in MeCN is 0.04 V vs. NHE. Using the equation, $E^\circ(\text{Os}^{\text{VI*}-\text{V}}) = E^\circ(\text{Os}^{\text{VI}-\text{V}}) + E_{0-0}$, the excited state is oxidizing with $E^\circ(\text{Os}^{\text{VI*}-\text{V}}) = 2.15 \text{ V vs. NHE}$. Upon excitation with UV-VIS light, **1** can oxidize saturated hydrocarbons such as cyclohexane, *n*-hexane, propane, adamantane and cumene. This features the first well defined metal-oxo complexes capable of oxidizing such unreactive C-H bonds. Results of photoreactions undertaken in MeCN or CH₂Cl₂ are summarized in Table 1. The organic products were either alcohols, ketones or aldehydes. The product yield for adamantane oxidation is low, presumably due to competitive secondary photochemical oxidation of the solvent by the excited osmium-oxo complex, the concentration of adamantane in CH₂Cl₂-MeCN being limited by its solubility. It is striking to find that the secondary C-H bonds of propane and primary C-H bonds of *n*-hexane could also be oxidized. Importantly, the oxidation of cyclohexane and *n*-hexane became catalytic in the presence of air. For cyclohexane oxidation, 16 turnovers were found after 12 h of reaction. The excited osmium-oxo species in this work has a significantly different reactivity from other highly oxidizing metal-oxo complexes. It is known that oxidation of adamantane by highly oxidizing Ru=O complexes takes place almost exclusively at the tertiary position.^{8,9} In this work, both secondary and tertiary C-H bonds of adamantane were photochemically oxidized by **1**. Fur-

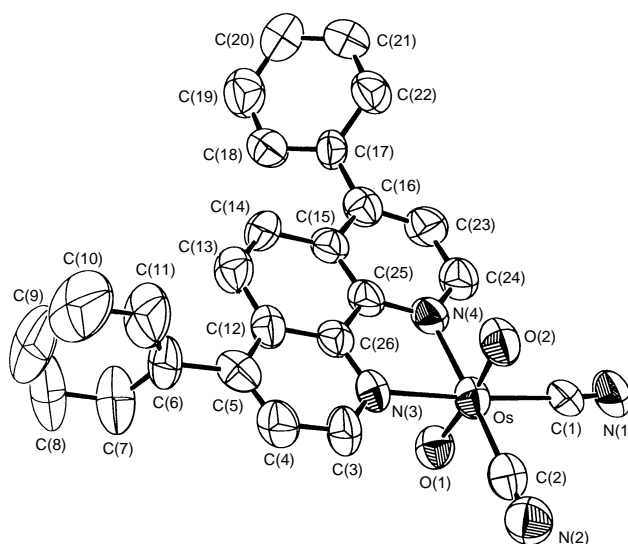


Fig. 1 Perspective view of **1** (50% thermal ellipsoids): Os-O(1) 1.721(5), Os-O(2) 1.723(6), Os-N(3) 2.127(7), Os-N(4) 2.157(6), Os-C(1) 2.02(1), Os-C(2) 2.053(8); O(1)-Os-O(2) 172.6(2), O(1)-Os-N(3) 87.0(2), O(1)-Os-C(1) 92.7(3), O(2)-Os-N(3) 87.5(3), O(2)-Os-C(1) 94.4(4), N(3)-Os-N(4) 77.5(2), N(3)-Os-C(1) 176.3(3), N(3)-Os-C(2) 95.3(3), C(1)-Os-C(2) 88.4(3)

Table 1 Photochemical oxidations of various organic substrates by **1**^a

Substrate	Solvent	Product(s)	Yield (%) (degassed)	Yield (%) (aerobic)
<i>n</i> -Hexane	MeCN (5 ml)– CH ₂ Cl ₂ (2 ml)	Hexan-3-one	26	160
		Hexan-2-one	32	195
		Hexan-3-ol	5	113
		Hexan-2-ol	10	171
		Hexaldehyde } Hexan-1-ol }	0.5	20
Cyclohexane	MeCN (5 ml)	Cyclohexanol	4	227 ^b
		Cyclohexanone	35	225
Cyclohexane	MeCN (5 ml)– CH ₂ Cl ₂ (2 ml)	Cyclohexanol	6	765 ^c
		Cyclohexanone	30	800
Propane	MeCN (4 ml)– propane (2 atm)	Propanone	16.4	
		Propan-2-ol	7.3	
Cumene	CH ₂ Cl ₂ (5 ml)	2-Phenylpropan-2-ol	115	
		Acetophenone	77	
Adamantane ^d	CH ₂ Cl ₂ (8 ml)– MeCN (2 ml)	1-Adamantanol	10.6	
		2-Adamantanol	10.2	

^a Complex **1** (30 mg for degassed and 10 mg for aerobic) was used with 5 ml of organic substrate; reaction time = 12 h. Yield based on **1** by GC analysis with an internal standard. ^b The yield for cyclohexanol and cyclohexanone after 2 days was 396 and 370%, respectively. ^c 2 atm O₂. ^d 0.2 g of adamantane used.

thermore, a small primary kinetic isotope effect (k_H/k_D) of *ca.* 2.2 was found for cyclohexane oxidation, which is smaller than that of 5.3 for [Ru^VL(O)]²⁺ {HL = [2-hydroxy-2-(2-pyridyl)ethyl]bis[2-(2-pyridylethyl)]amine}.¹⁰ The small kinetic isotopic effect and the lower tertiary C–H/secondary C–H selectivity suggests that the excited Os=O species could be regarded as a highly reactive ‘ligated oxygen atom’ species and Sawyer used the term ‘oxene’ to denote such a species.¹¹ A trace amount of cyclohexyl chloride was detected in the photochemical oxidation of cyclohexane in the presence of CCl₄.

An orange–brown solution was usually obtained after the photochemical reactions of **1** in MeCN, which slowly re-oxidized back to **1** by air. Interestingly, it gave an intense orange emission at 590 nm, the intensity of which is 20 times higher than the emission of **1** recorded under similar conditions. Our previous study revealed that [Os^{II}(CN)₂(X)₂L] complexes are highly emissive (quantum yield = 0.4–0.06) at similar energy (L = dpphen; λ_{\max}/nm , X = Me₂SO, 625; PPh₃, 660).¹² We tentatively assign the photoproduct as [Os^{II}(CN)₂(dpphen)(MeCN)₂]. It is likely that the coordinated MeCN in [Os^{II}(CN)₂(dpphen)(MeCN)₂] is more labile than in *trans*-[Os^{II}(tmc)(MeCN)₂]²⁺, thus accounting the observed aerobic reoxidation of the former back to the starting *trans*-dioxoosmium(VI) complex. For the aerobic photochemical oxidations, there could be other reactive pathway(s) besides the one by the excited osmium–oxo species, since the cyclohexanone/cyclohexanol ratio for the aerobic and anaerobic oxidation of cyclohexane are different (1 : 1 *cf.* 10 : 1).

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Footnotes

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† Proton NMR (CDCl₃): δ 10.17 (d, 2), 8.24 (s, 2), 8.10 (d, 2), 7.69–7.52 (m, 5). IR (Nujol): ν (Os=O) 856.1 cm⁻¹. UV–VIS: λ/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), 290 (35 835), 330(sh) (8492), 367(sh) (966).

‡ Crystal data: C₂₆H₁₆N₄O₂Os, M_r = 606.64, orthorhombic, space group *Pbca* (no. 61), a = 27.385(4), b = 13.025(2), c = 12.635(2) Å, U = 4508(1) Å³, Z = 8, D_c = 1.788 g cm⁻³, $\mu(\text{Mo-K}\alpha)$ = 56.86 cm⁻¹, $F(000)$ = 2336, T = 301 K. A brown crystal of dimensions 0.20 × 0.15 × 0.30 mm

was used for data collection on a Rigaku AFC7R diffractometer with graphite monochromatized Mo-K α radiation (λ = 0.71073 Å) using ω -2 θ scans with ω -scan angle (0.63 + 0.35 tan θ)° at a scan speed of 4.0 min⁻¹. 4452 reflections were uniquely measured, of which 2307 reflections with $I > 1.5\sigma(I)$ were considered observed and used in the structural analysis. A crystallographic asymmetric unit consists of one molecule and all 33 non-H atoms were refined anisotropically. 16 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 298 variable parameters by least-squares refinement on F with $\omega = 4 F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.018F_o^2)^2]$ for 2307 reflections with $I > 1.5\sigma(I)$ was reached at $R = 0.035$ and $R_w = 0.030$ with a goodness-of-fit of 1.32 ($\Delta/\sigma_{\max} = 0.01$). CCDC 182/509.

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