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Heterobimetallic nitrido-bridged Ru(II)NOs(VIII) and Ru(II)NOs(VI) complexes containing ruthenium porphyrins

Wa-Hung Leung ^{a,*}, Joyce L.C. Chim ^a, Willetta Lai ^a, Leo Lam ^a, Wing-Tak Wong ^{b,1}, Wing Hang Chan ^c, Chi-Hung Yeung ^c

^a Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong ^b Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

^c Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hunghom, Kowloon, Hong Kong

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Abstract

Treatment of Ru(por)(NO)(OTf) (por = dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin H₂(OEP) or 5,10,15,20-tetra(*p*-tolyl)porphyrin H₂(TTP), OTf = triflate) with [NⁿBu₄][OsO₃N] afforded the nitrido-bridged Ru(II)–Os(VIII) complexes [(por)(NO)RuNOsO₃] (por = OEP (**3**) or TTP (**4**)). The structure of **3** has been established by X-ray crystallography. The Ru–N(O), Ru–N(Os) and Os–N distances in **3** are 1.83(2), 2.03(1) and 1.79(1) Å, respectively; the Ru–N–O and Ru–N–Os angles are 153(1) and 138.4(8)°, respectively. Reaction of Ru(por)(NO)(OTf) with [NⁿBu₄][OsNL₂] (H₂L = 3,4-toluenedithiol) gave the nitrido-bridged Ru(II)–Os(VI) complexes (por)(NO)RuNOsL₂ (por = OEP (**5**), TTP (**6**)). Treatment of Ru(OEP)(NO)(OTf) with ReN(Et₂dtc)₂ (Et₂dtc = *N*,*N*-diethyldithiocarbamate) afforded the Ru(II)–Re(V) complex (OEP)(NO)RuNRe(Et₂dtc)₂(OTf) (**7**). Complexes **3** and **4** exhibit porphyrin-centered oxidation along with Os(VIII)–Os(VII) and Ru(II)–Ru(I) reductions. Complexes **5** and **6** exhibit Os(VII)–Os(VI) and porphyrin ring oxidation along with Ru(II)–Ru(I) reduction. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Ruthenium complexes; Osmium complexes; Nitrido-bridged complexes; Porphyrin complexes

1. Introduction

Heterobinuclear complexes containing metalloporphyrins are of interest because of their rich electrochemistry and their potential application in multi-electron redox catalysis. While mixed-ligand μ -oxo bridged heterobimetallic complexes of the type (por)MOM'L (M = Cr [1], Fe [2], or Ru [3]; M' = transition metal; por = porphyrin dianion; L = non-porphyrin ligand) are well documented, there are relatively few examples of the nitrido-bridged analogues. Nitrido-bridged metal porphyrins $[Fe(TPP)]_2(m-N)$ (TPP = 5,10,15,20-tetraphenylporphyrin dianion) [4], (por)FeNFe(pc) [5,6] and (por)FeNRu(pc) [6] (pc = phthalocyanine dianion) have been isolated and implicated as the intermediates for the intermetal nitrogen atom transfer reactions of metalloporphyrins [7]. Previously we reported that μ -nitridobridged complexes Os(VIII)NM (M = Au, Pt, Ir) [8] and $O_{s}(VI)NM (M = Au, Ir) [9]$ can be prepared conveniently by reactions of cationic organometallic complexes with $[Os(VIII)O_3N]^-$ and $[Os(VI)NL_2]^ (H_2L = 3,4$ toluenedithiol), respectively. This prompted us to synthesize the analogous complexes of metalloporphyrins using the same methodology. Nitrosylruthenium(II) porphyrins were chosen to be nitride acceptors because they are known to bind to π -donor ligands such as alkoxides [10,11], thiolates [11,12], and hydroxide [13]. We here describe the reactions of nitrosylruthenium(II) porphyrins with nitrido-Os and -Re complexes

^{*} Corresponding author. Tel.: + 852-2358 7359; fax: + 852-2358 1594.

E-mail address: chleung@ust.hk (W.-H. Leung)

 $^{^{\}rm l}$ To whom all crystallographic correspondence should be addressed.

and the characterization of the resulting bimetallic $\mu\text{-ni-tride}$ complexes.

2. Experimental

2.1. General

Solvents were purified and distilled prior to use. ¹H NMR spectra were recorded on a Bruker ALX 300 spectrometer operating at 300 MHz, chemical shifts (δ) were reported with reference to SiMe₄. Infrared spectra (Nujol) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer, UV-visible spectra on a Milton Roy Spectronic 3000 diode-array spectrophotometer. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) Model 273A potentiostat, the working and reference electrodes were glassy carbon and Ag–AgNO₃ (0.1 M in acetonitrile), respectively. Potentials were reported with reference to ferrocenium–ferrocene (Cp₂Fe^{+/0}). Elemental analyses were performed by Medac, Surrey, UK.

The porphyrins Ru(por)(NO)Cl (por = dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin H₂(OEP) or 5,10,15,20-tetra(*p*-tolyl)porphyrin H₂TTP) [14], [NⁿBu₄][OsO₃N] [15], and ReN(Et₂dtc)₂ (Et₂dtc = N,N'-diethyldithiocarbamate) [16] were prepared according to the literature methods. [NⁿBu₄][OsNL₂] was prepared from [NⁿBu₄][OsNCl₄] [17] and H₂L (3,4-toluenedithiol, Strem) according to Sellmann's procedure [9,18]. Hydrogen atomic labeling schemes for the porphyrins and L are shown in Scheme 1.

2.2. Synthesis

2.2.1. Ru(por)(NO)(OTf) (por = OEP (1), TTP(2))

To a solution of Ru(por)(NO)Cl (100 mg) in CH_2Cl_2 (10 ml) was added 1 equiv. of AgOTf and the mixture was stirred at room temperature overnight. The solvent

was pumped off and the residue recrystallized from CH_2Cl_2 -hexane to give a purple solid. Yield 70-80%.

2.2.2. Spectroscopic data for 1

¹H NMR (CDCl₃): δ 2.03 (t, J = 7.7 Hz, 24H, CH₃), 4.24 (q, J = 7.7 Hz, 16H, CH₂), 10.53 (s, 4H, *meso*-H). λ_{max} (CH₂Cl₂): 391 (Soret) nm. IR (Nujol): ν (cm⁻¹), 1854 [ν (NO)], 1285 and 1277 [ν (SO)]

2.2.3. Spectroscopic data for 2

¹H NMR (CDCl₃): δ 2.74 (s, 12H, *p*-Me), 7.58 (d, J = 7.5 Hz, 4H, H_o), 7.63 (d, J = 7.5 Hz, 4H, H_o), 8.15 (d, J = 7.5 Hz, 4H, H_m), 8.19 (d, J = 7.5 Hz, 4H, H'_m), 9.16 (s, 8H, H_b). λ_{max} (CH₂Cl₂): 411 (Soret) nm. IR (Nujol): ν (cm⁻¹), 1870 [ν (NO)], 1287 and 1250 [ν (SO)].

2.2.4. (OEP)(NO)RuNOsO₃ (3)

To a solution of Ru(OEP)(NO)(OTf) (100 mg, 0.143 mmol) in CH₂Cl₂ (20 ml) was added [NⁿBu₄][OsO₃N] (68 mg, 0.143 mmol) and the mixture was stirred at room temperature for 30 min. The solvent was pumped off and the residue was recrystallized from CH₂Cl₂-hexane to give purple crystals. Yield: 100 mg (76%). *Anal.* Calc. for C₃₆H₄₄N₆O₄OsRu: C, 47.2; H, 4.8; N, 9.2. Found: C, 47.2; H, 5.1; N, 8.8%. ¹H NMR (CDCl₃): δ 2.01 (t, J = 7.6 Hz, 12H, CH₃), 2.03 (t, J = 7.6 Hz, 12H, CH₃), 4.21 (q, J = 7.6 Hz, 8H, CH₂), 4.22 (q, J = 7.6 Hz, 8H, CH₂), 10.42 and 10.44 (s, 4H, *meso*-H). IR (Nujol): ν (cm⁻¹), 894 and 908 [ν (Os=O)], 1842 [ν (N=O)]. λ_{max} (CH₂Cl₂): 396 (Soret), 487 sh, 572 sh nm.

2.2.5. (TTP)(NO)RuNOsO₃ (4)

This was prepared as for **1** from Ru(TTP)(NO)(OTf) (100 mg) and [NⁿBu₄][OsO₃N] (68 mg) in CH₂Cl₂ (10 ml) and recrystallized from CH₂Cl₂–MeCN. Yield: 90 mg (60%). *Anal.* Calc. for C₄₈H₃₆N₆O₄OsRu: C, 54.8; H, 3.4; N, 8.0. Found: C, 54.2; H, 3.6; N, 7.7%. ¹H NMR (CDCl₃): δ 2.73 (s, 12H, *p*-Me), 7.60 (d, *J* = 8.1 Hz, 8H, H_m), 8.17 (d, *J* = 8.1 Hz, 8H, H_o), 9.08 (s, 8H,



Scheme 1.

Table 1			
Crystallographic of	lata for (OEP)(NO)Rul	$NOsO_3$ (3)

Empirical formula M Crystal system Colour Habit Crystal dimension (mm) λ (Å)	$\begin{array}{l} C_{36}H_{44}N_6O_4OsRu\\ 916.05\\ triclinic\\ black\\ plate\\ 0.16 \times 0.26 \times 0.28\\ 0.71073 \end{array}$
Space group	P1 (No. 2)
a (Å)	10.279(1)
b (Å)	11.010(1)
c (Å)	16.329(1)
α (°)	99.13(2)
β (°)	95.07(2)
γ (°)	97.33(2)
V (Å ³)	1798.5(4)
Ζ	2
$D_{\rm c} ~({\rm g}~{\rm cm}^{-3})$	1.691
Scan type	ω –2 θ
μ (Mo K α) (cm ⁻¹)	39.94
No. of reflections	4995
Observed reflections $(I > 3.00\sigma(I))$	793
Weighing scheme	$1/\sigma^2(F)$
R ^a	0.057
R _w ^b	0.079
<i>F</i> (000)	908
Goodness-of-fit ^c	1.94

^a $R = (\Sigma ||F_o| - |F_c||) / \Sigma |F_o|.$

^b $R_w = [\Sigma(w|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}.$

^c Goodness-of-fit = $[(\Sigma w |F_o| - |F_c|)^2 / \Sigma N_{obs} - N_{param}]^{1/2}$.

H_b). IR (Nujol): ν (cm⁻¹) 898 and 904 [ν (Os=O)], 1856 [ν (N=O)]. λ_{max} (CH₂Cl₂): 329, 416 (Soret) nm.

2.2.6. (OEP)(NO)RuNOsL₂ (5)

To a solution of Ru(OEP)(NO)(OTf) (65 mg, 0.08 mmol) in CH₂Cl₂ (20 ml) was added 1 equiv. of [NⁿBu₄][OsNL₂] (60 mg, 0.08 mmol) and the mixture was stirred at room temperature overnight. The solvent was pumped off and the residue extracted with ether. Addition of hexane and slow evaporation in air afforded dark crystals. Yield: 30 mg (32%). *Anal.* Calc. for C₅₀H₅₆N₆OS₄OsRu: C, 51.1; H, 4.8; N, 7.2. Found: C, 50.9; H, 5.1; N, 6.8%. ¹H NMR (CDCl₃): δ 1.91–1.96 (overlapping t, 24H, CH₃), 2.32 (s, 6H, Me of L), 4.00–4.17 (overlapping q, 16H, CH₂), 6.57 (d, *J* = 7.8 Hz, 2H, H_m of L), 6.71 (s, 2H, H_o of L), 6.81 (d, *J* = 7.8 Hz, 2H, H'_o of L), 10.12 (s, 4H, *meso*-H). λ_{max} (CH₂Cl₂): 397 (Soret), 494, 529 nm. IR (Nujol): ν (cm⁻¹), 1842 [ν (N=O)].

2.2.7. (TTP)(NO)RuNOsL₂ (6)

This was prepared as for **3** from Ru(TTP)(NO)(OTf) (80 mg, 0.08 mmol) and [NⁿBu₄][OsNL₂] (64 mg, 0.08 mmol) and recrystallized from CH₂Cl₂–MeCN. Yield: 55 mg (50%). *Anal.* Calc. for C₆₂H₄₈N₆OS₄OsRu: C, 56.8; H, 3.7; N, 6.4. Found: C, 47.2; H, 5.1; N, 8.8%.

¹H NMR (CDCl₃): δ 2.29 (s br, 6H, Me of L), 2.74 (s br, 12H, *p*-Me), 6.60 (dd, J = 7.8 Hz, J' = 3.0 Hz, 2H, H_m of L), 6.83 (s, 1H, H_o of L), 6.85 (s, 1H, H_o of L), 6.89 (dd, J = 7.8 Hz, J' = 3.0 Hz, 2H, H'_o of L), 7.52–8.11 (m, 16H, H_o and H_m of ttp), 8.79–8.88 (m, 8H, H_b). λ_{max} (CH₂Cl₂): 418 (Soret) nm. IR (Nujol): ν (cm⁻¹), 1848 [ν (N=O)].

2.2.8. $(OEP)(NO)RuNRe(Et_2dtc)_2(OTf)$ (7)

To a solution of **1** (70 mg, 0.09 mmol) in CH₂Cl₂ (10 ml) was added ReN(Et₂dtc)₂ (50 mg, 0.09 mmol) in CH₂Cl₂ (10 ml) and the reaction mixture was stirred at room temperature overnight. The solvent evaporated to dryness and the residue recrystallized from CH₂Cl₂-hexane to give a dark purple solid. Yield: 80 mg (71%). *Anal.* Calc. for C₄₇H₆₄N₈O₄F₃S₅ReRu·CH₂Cl₂: C, 41.3; H, 4.7; N, 8.0. Found: C, 40.7, H, 4.7; N, 8.2%. ¹H NMR (CDCl₃): δ 0.99 (t, J = 7.2 Hz, 12H, CH₃ of Et₂dtc), 2.00 (t, J = 7.5 Hz, 24H, CH₃), 3.07 (m, 4H, CH₂ of Et₂dtc), 3.24 (m, 4H, CH₂ of Et₂dtc), 4.21 (q, J = 7.5 Hz, 16H, CH₂), 10.38 (s, 4H, *meso*-H). IR (Nujol): ν (cm⁻¹), 1856 [ν (NO)]. λ_{max} (CH₂Cl₂): 296, 399 (Soret) nm, 518 nm.

2.3. X-ray crystallography

A summary of crystal data and experimental details for 3 is listed in Table 1. X-ray quality crystals of 3 were grown from a CH₂Cl₂-hexane solution in air at room temperature. Diffraction measurements were performed with a MAR-Research Image Plate diffractometer with graphite monochromated Mo Ka radiation at room temperature. All intensity data were corrected for Lorentz polarization effect. An approximation to absorption correction by inter-image scaling was also applied. The structure was solved by direct methods and refined by full-matrix least-squares analysis. All calculations were performed using the teXan [19] crystallographic software package. The maximum and minimum peaks on the final difference Fourier map correspond to 1.63 and -0.92 e ${\rm \AA}^{-3},$ respectively. The fractional atomic coordinates for 3 are listed in Table 2.

3. Results and discussion

3.1. Synthesis and characterization of Ru(II)NOs(VIII) complexes

Reaction of Ru(por)(NO)Cl with an equimolar amount of AgOTf gave Ru(por)(NO)(OTf) (por = OEP (1), TTP (2)). The observation of the splitting of v(SO)at ca. 1260 cm⁻¹ indicates that the triflate is bound to metal for 1 and 2 [20]. The triflate in 1 and 2 is labile and can be displaced easily by metal nitrides. Thus,

Complexes 3 and 4 are stable in both the solid state and solutions. NMR spectroscopy reveals no signs of osmate ligand dissociation for 3 and 4 in $CDCl_3$. The v(Os=O) for 3 (898 and 904 cm⁻¹) are higher than those for free $[OsO_3N]^-$ (871 and 891 cm⁻¹), indicating that upon coordination to Ru the Os-oxo bonds in

Table 2

Final	atomic	coordinates	for	(OEP)(NO)RuNOsO3	3
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Atom	x	у	Ζ
Os(1)	-0.51174(10)	-0.21210(9)	-0.31088(6)
Ru(1)	0.2225(2)	0.0027(1)	-0.22775(9)
O(1)	-0.628(2)	-0.288(2)	-0.263(1)
O(2)	0.585(2)	0.140(2)	0.384(1)
O(3)	0.433(2)	0.320(2)	0.361(1)
O(4)	0.0192(10)	0.1966(10)	-0.2061(6)
N(1)	-0.255(1)	0.067(1)	0.1077(9)
N(2)	0.323(1)	0.139(1)	-0.2690(9)
N(3)	-0.208(1)	0.075(1)	-0.3497(9)
N(4)	-0.146(1)	0.143(1)	-0.1886(10)
N(5)	0.402(1)	0.102(1)	-0.2352(8)
N(6)	0.059(2)	0.096(2)	0.217(1)
C(1)	0.218(2)	0.019(2)	0.037(1)
C(2)	0.253(2)	0.097(2)	0.035(1)
C(3)	0.231(2)	0.071(2)	0.124(1)
C(4)	0.336(2)	0.028(2)	0.144(1)
C(5)	0.310(2)	0.192(2)	0.009(1)
C(6)	0.363(2)	0.296(2)	0.058(1)
C(7)	0.509(2)	0.271(2)	0.061(1)
C(8)	-0.312(2)	0.174(2)	-0.081(1)
C(9)	0.359(2)	0.247(2)	0.132(1)
C(10)	0.370(2)	0.229(2)	0.219(1)
C(11)	0.427(2)	0.310(2)	-0.271(1)
C(12)	0.494(2)	0.420(2)	0.239(1)
C(13)	-0.632(2)	0.386(2)	-0.217(2)
C(14)	-0.413(2)	0.264(2)	-0.3.51(1)
C(15)	-0.457(2)	0.310(2)	-0.429(1)
C(16)	-0.349(2)	0.396(2)	-0.454(1)
C(17)	0.346(2)	0.152(2)	-0.3.50(1)
C(18)	0.315(2)	0.075(2)	-0.418(1)
C(19)	0.249(2)	-0.031(2)	-0.419(1)
C(20)	0.222(2)	-0.111(2)	-0.492(1)
C(21)	0.250(2)	-0.090(2)	-0.582(1)
C(22)	-0.147(2)	-0.004(3)	-0.608(2)
C(23)	-0.165(2)	-0.205(2)	-0.465(1)
C(24)	-0.133(3)	-0.320(3)	0.518(1)
C(25)	0.003(4)	-0.309(3)	0.529(2)
C(26)	-0.155(2)	0.181(2)	-0.377(1)
C(27)	-0.103(2)	-0.254(2)	0.323(1)
C(28)	-0.099(2)	0.239(2)	0.237(1)
C(29)	0.046(2)	-0.319(2)	-0.185(1)
C(30)	0.020(2)	-0.430(2)	-0.216(1)
C(31)	-0.076(3)	-0.540(3)	-0.236(2)
C(32)	0.064(2)	0.274(2)	-0.107(1)
C(33)	-0.034(2)	0.321(2)	-0.026(1)
C(34)	-0.156(2)	0.389(2)	0.003(2)
C(35)	0.127(2)	-0.161(2)	-0.107(1)
C(36)	-0.159(2)	-0.087(2)	0.039(1)

 $[NOsO_3]^-$ are strengthened apparently due to weakening of the Os-nitride bond (see later). The v(Os=N) was

not assigned due to the presence of porphyrin bands in the 1000-1100 cm⁻¹ region. The solid-state structure of **3** has been established by X-ray crystallography. Fig. 1 shows a perspective view of 3; selected bond lengths and angles are listed in Tables 3 and 4. Unlike the other structurally characterized nitrosylruthenium(II) porphyrins, the Ru–N–O linkage in 3 is bent at an angle of 153(1)°. Although the Ru-N-O angle for 3 is comparable to that for $Ru(TTP)(NO)(C_6H_5F-p)$ (152°) [21], the v(N=0) for the former (1854 cm⁻¹) is considerably higher than that for the latter (1773 cm^{-1}) [21]. The Ru–N(O) distance for **3** of 1.83(2) Å is within the range expected for nitrosylruthenium(II) porphyrins (ca. 1.72–1.79 Å) [10–13]. The Ru–N(Os) bond in **3** is relatively short (2.03(1) Å) and is comparable to the Ru(IV)-amide bond in Ru(TPP)(NHTs)(pz) (Ts = tosyl, pz = pyrazolyl) (2.025(11) Å) [22], suggestive of π -bonding in Ru–N(Os). The Ru–N(Os) distance is, however, longer than those for symmetric µ-nitrido diruthenium complexes (1.718–1.744 Å) [23]. The existence of π bonding in Ru–N(Os) for **3** is also evidenced in its solution ¹H NMR spectrum, which displays magnetically non-equivalent methyl and meso proton signals. Apparently, the low-lying vacant nitrosyl π^* molecular orbitals interact extensively with the filled Ru $d\pi$ orbitals, rendering the $p\pi[N(Os)] - d\pi(Ru)$ interaction possible, as suggested for the related trans-[Ru^{II}(CO)X] (X = π -donor ligand) system [24]. It is noteworthy that the Os–N(Ru) bond in 3 (1.79(1) Å) is significantly longer than those for $[OsO_3N]^-$ (1.67(2) Å) [25], (PPh₃)AuNOsO₃ (1.69 (2) Å) [8] and organoimido-Os(VIII) complexes (e.g. 1.697(4) Å for $OsO_3(NC_{10}H_{15}), C_{10}H_{15} = 1$ -adamantyl) [26] and, to our knowledge, is the longest Os(VIII)-nitride bond reported so far. This suggests a formal double bond between Os and nitride and the bonding in 3 is best described as Ru-N=Os. Apparently, the decrease in Os-N bond order from three to two is compensated for by the strengthening of the Ru-N(Os) and Os=O bonds. In contrast to the donor-acceptor type µ-nitrido Os(VIII) complexes, e.g. (PPh₃)AuNOsO₃, and organoimido-Os(VIII) complexes (RN)OsO₃, which contain essentially linear M(R)-N=Os linkages, the Ru-N=Os in 3 is bent at an angle of $138.4(2)^{\circ}$. It might be noted that a similar bent, asymmetric μ^2 bridging mode of nitride has been observed for $[NW{OC(CH_3)_2CF_3}_3]_3$, which contains an alternation of long and short W-N bonds within the six-membered W₃N₃ ring [27]. The W-N=W angle in $[NW{OC(CH_3)_2CF_3}_3]_3$ (average 152.9°) is larger than that in **3** probably due to steric effects. Interestingly the dihedral angle between Ru-N-Os and Ru-N-O in 3 is ca. 114.04°, indicating that different Ru $d\pi$ orbitals are used for the Ru-NO backbonding and Ru-N(Os)



Fig. 1. Perspective view of (OEP)(NO)RuNOsO₃ (3).

 π -bonding. This geometry may be rationalized in terms of maximization of the overlap between the nitrosyl π^* molecular orbital, which is perpendicular to the Ru–N–O plane, and the 'lone pair' on the sp² hybridized nitride, which lies on the Ru–N–Os plane.



The anion $[OsO_3N]^-$ was found to react with other unsaturated metalloporphyrins such as chromium(III) porphyrins. For example, addition of $[OsO_3N]^-$ to Cr(OEP)(OTf) led to the formation a new species, presumably nitride-bridged (OEP)CrNOsO₃, as evidenced by UV–Vis spectroscopy. Intermetal nitrogen atom transfer from Os to Cr was not observed. The IR spectrum of this species shows the upshift of v(Os=O) to 910 cm⁻¹, suggesting that the Os=O bonds are strengthened upon the complex formation. This Cr–Os species does not react with alkenes but reacts readily with PPh₃. Attempts to crystallize this Cr(III)–Os(VIII) species led to isolation of an intractable oil.

3.1.1. Synthesis and characterization of Ru(II)NOs(VI) and Ru(II)NRe(V) complexes

Treatment of Ru(por)(NO)(OTf) with $[N^nBu_4]$ -[OsNL₂] (H₂L = 3,4-toluenedithiol) afforded the Ru(II)-Os(VI) complexes (por)(NO)RuNOsL₂ (por = OEP (5), TTP (6)) (Scheme 3).

NMR spectroscopy indicates that complexes 5 and 6 are stable with respect to ligand dissociation in solutions. The observation of an unsymmetrical ¹H NMR spectrum for 5 is indicative of Ru–N(Os) multiple bond character. Although crystal structures are not available, it seems unlikely that the Ru–N–Os in these complexes is bent, as found in 3, in light of the steric demand of the dithiolate ligand L. The v(N=O) for 3 is similar to

Table 3 Selected bond lengths (Å) and angles (°) for (OEP)(NO)RuNOsO₂ **3**

Bond lengths (Å)			
Os(1)–O(1)	1.69(2)	Os(1)–O(2)	1.71(1)
Os(1)–O(3)	1.67(2)	Os(1)–N(5)	1.79(1)
Ru(1)-N(1)	2.05(1)	Ru(1)-N(2)	2.08(1)
Ru(1)–N(3)	2.06(1)	Ru(1) - N(4)	2.08(4)
Ru(1) - N(5)	2.03(1)	Ru(1)–N(6)	1.83(2)
O(4)–N(6)	1.26(2)		
Bond angles (°)			
O(1)–Os(1)–O(2)	110(1)	O(1)-Os(1)-O(3)	106(1)
O(1)–Os(1)–N(5)	109.8(7)	O(2) - Os(1) - O(3)	107(1)
O(2)-Os(1)-N(5)	110.8(8)	O(3)–Os(1)–N(5)	111.7(8)
N(1)-Ru(1)-N(2)	89.8(5)	N(1)-Ru(1)-N(3)	174.0(6)
N(1)-Ru(1)-N(4)	89.8(6)	N(1)-Ru(1)-N(5)	84.9(5)
N(1)-Ru(1)-N(6)	93.6(7)	N(2)-Ru(1)-N(3)	90.2(6)
N(2)-Ru(1)-N(4)	173.3(6)	N(2)-Ru(1)-N(5)	86.8(5)
N(2)-Ru(1)-N(6)	94.7(6)	N(3)-Ru(1)-N(4)	89.5(6)
N(3)-Ru(1)-N(5)	89.1(6)	N(3)-Ru(1)-N(6)	92.5(7)
N(4)-Ru(1)-N(5)	86.5(6)	N(4)-Ru(1)-N(6)	92.0(6)
N(5)-Ru(1)-N(6)	177.8(6)	Os(1) - N(5) - Ru(1)	138.4(8)
Ru(1)–N(6)–O(4)	153(1)		



Fig. 2. Cyclic voltammograms of (a) (OEP)(NO)RuNOsO₃ (3) and (b) (OEP)(NO)RuNOsL₂ (5) in CH₂Cl₂ at a glassy carbon electrode; scan rate = 100 mV s^{-1} .

$$\rightarrow [(OEP^{\bullet}^{+})(NO)RuNOsO_{3}]^{+}$$
(1)

 $[OsO_3N]^-$ and $[OsNL_2]^-$ is comparable. Similarly reaction of Ru(OEP)(NO)(OTf) with ReN-(Et₂dtc)₂ afforded the RuNRe complex (OEP) (NO)RuNRe(Et₂dtc)₂(OTf) (7). Unlike 5, the ¹H NMR spectrum for 7 is symmetric with one singlet for the *meso* protons, indicating that the ReN(Et₂dtc)₂

moiety is rotating freely around the Ru–N bond on the NMR time scale. The IR spectrum for 7 shows the NO band at 1856 cm⁻¹, which is higher than those for 3 and 5.

that for 5, suggesting that the donor strength of

3.2. Electrochemistry

The cyclic voltammogram (CV) of complex **3** in CH_2Cl_2 (Fig. 2a) exhibits a reversible oxidation couple at 0.55 V, which is assigned as the porphyrin-centered oxidation (Eq. (1)).

$[(OEP)(NO)Ru(II)NOs(VIII)O_3] - e^{-1}$

This potential is comparable to those found for Ru(OEP)(NO)(OTf) (0.68 V) and [Ru(TTP)(NO)-(OH₂)]⁺ (1.26 V vs. standard calomel electrode) [28]. The corresponding oxidation for 4 (0.72 V) is more anodic than that for 3, consistent with the relative ease of oxidation for porphyrin macrocycle OEP > TTP. Electroreduction of 3 occurs at -1.10, -1.33 and -1.77 V. The irreversible reduction at -1.11 V is assigned tentatively as the Ru(II)-Ru(I) reduction (Eq. (2)) because a similar reduction potential was found for Ru(OEP)(NO)(OTf).

$$[(OEP)(NO)Ru(II)NOs(VIII)O_3] + e^{-}$$

$$\rightarrow [(OEP)(NO)Ru(I)NOs(VIII)O_3]^{-}$$
(2)

Consistent with this assignment, the corresponding reduction for the less electron-rich TTP analogue 4 was found at a less negative potential (-0.88 V). The irreversible reduction couple at -1.33 V for 3 is tenta-





tively assigned as the Os-centered reduction (Eq. (3)) because a similar reduction was found for 4 (at -1.22 V).

$$[(OEP)(NO)Ru(II)NOs(VIII)O_3] + e^{-}$$

$$\rightarrow [(OEP)(NO)Ru(II)NOs(VII)O_3]^{-}$$
(3)

The Os(VIII) – Os(VII) reductions for **3** and **4** occur at less negative potentials than that for $[OsO_3N]^-$ (-1.45 V), indicative of Ru to Os charge delocalization in these complexes. The nature of the irreversible reduction at -1.77 V is not clear.

The CV of **5** in CH₂Cl₂ (Fig. 2b) shows reversible oxidation couples at 0.49 and 0.75 V and irreversible reduction waves at -1.11 and -1.25 V. The oxidation couple at 0.49 V is assigned as the Os-centered oxidation (Eq. (4)) because [OsNL₂]⁻ was found to be oxidized at 0.39 V.

$$[(OEP)(NO)Ru(II)NOs(VI)O_3] - e^{-1}$$

$$\rightarrow [(OEP)(NO)Ru(II)NOs(VII)O_3]^+$$
(4)

The Os(VII)–Os(VI) potential for **5** is more positive than that for $[OsNL_2]^-$, suggesting that there is charge delocalization from Os to Ru in **5**. Fig. 3 shows the spectral trace for the reaction of **5** with $(NH_4)_2[Ce(NO_3)_6]$. Upon addition of ca. 1 equiv. of Ce(IV), a new species with the Soret band at ca. 392 nm (presumably the Ru(II)–Os(VII) complex) appears. Attempts to isolate this species by stoichiometric oxidation of **5** with Ag(OTf) in a preparative scale were unsuccessful. The second oxidation couple for **5** at 0.75 V was assigned as the porphyrin centered oxidation Eq. (5).

$$[(OEP)(NO)Ru(II)NOs(VII)L_2]^+ - e^-$$

$$\rightarrow [(OEP^{\bullet +})(NO)Ru(II)NOs(VII)L_2]^{2+}$$
(5)

The porphyrin ring oxidation for **5** is more anodic than that for **1** because the former involves removal of electron from a cation rather than a neutral species. The irreversible reduction at -1.11 V is assigned tentatively as the Ru(II)-Ru(I) reduction by comparison with the electroreduction of **3**. The nature of the irreversible reduction at -1.25 V is not clear.

In summary, we have demonstrated that $[Ru(por)-(NO)]^+$ are capable of forming stable nitrido-bridged complexes with $[OsO_3N]^-$, $[OsNL_2]^-$ and ReN $(Et_2dtc)_2$. X-ray crystallography indicates multiple bond character of Ru(II)-N(Os) in 3. The structural data are consistent with the formulation of the asymmetric nitride bridge (Ru-N=Os) for these complexes, which is in contrast to the previously reported donor-acceptor type nitride bridges (e.g. $M \leftarrow N=Os$) [8]. Electronic communication between Ru and Os center was observed for these nitrido-bridged Ru(II)-Os(VII) and Ru(II)-Os(VI) complexes.



Fig. 3. Spectral trace for the oxidation of $(OEP)(NO)RuNOsL_2$ (5) with Ce(IV) in CH₂Cl₂.

Table 4 Formal potentials (E°) for the nitrido-bridged ruthenium porphyrins^a

Complex	E° (V vs. $Cp_2Fe^{+/0}$)	
	Oxidation	Reduction
(OEP)(NO)RuNOsO ₃ (TTP)(NO)RuNOsO ₃ Ru(OEP)(NO)(OTf) [OsO ₃ N] ⁻ (OEP)(NO)RuNOsL ₂ [OsNL ₂] ⁻	0.55 0.72 0.68 0.49, 0.75 0.39	$\begin{array}{c} -1.11^{\rm b}, -1.33, -1.77^{\rm b} \\ -0.88^{\rm b}, -1.22 \\ -0.93^{\rm b} \\ -1.45^{\rm b} \\ -1.11^{\rm b}, -1.25^{\rm b} \end{array}$

^a Potentials measured at a glassy carbon electrode in CH_2Cl_2 using 0.1 M [NⁿBu₄](PF₆) as supporting electrolyte. Scan rate = 100 mV s⁻¹.

^b Irreversible.

4. Supplementary material

Supplementary material containing listings of atomic coordinate and thermal parameters, final atomic coordinates, and bond distances and angles is available from the author (Wing-Tak Wong) on request.

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