

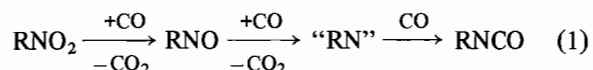
## Nitrosobenzene Complexes of (Octaethylporphinato)-ruthenium(II)

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Our interest in the use of nitroso compounds as potential substrates for acid-promoted oxidation by  $O_2$  using ruthenium(II) porphyrins as catalysts [1, 2], and reports on the use of metalloporphyrins as catalysts for the carbonylation of nitro compounds to organic isocyanates [3, 4], have led us to study the interaction of nitrosobenzene with (octaethylporphinato)ruthenium(II) species. In catalytic carbonylation of nitro compounds more generally, nitroso species, formed by deoxygenation of the  $NO_2$  group by CO, are usually considered as intermediates en route to nitrenes that are finally carbonylated to the isocyanate [3, 5]:



The metal complex-catalyzed processes outlined in reaction (1) are not well defined mechanistically, and a study of the coordination chemistry of the various species should lead to a better insight into the catalysis, and perhaps to novel reactivity. This is particularly so for metalloporphyrins where the planar  $N_4$ -donor set is incompatible with the “oxidative–addition, insertion, reductive elimination, 2-electron step” type of catalysis; indeed, metalloporphyrin-catalyzed organometallic reactions are often found to operate via radical processes [6–8]. Further, nitrosobenzene is known to coordinate at the heme centre of myoglobin and hemoglobin [9], but remarkably little has been reported on interaction of such nitroso ligands with protein-free metalloporphyrins. Structural and spectroscopic work [10] on  $Fe(\text{porp})(RNO)L$  species (where  $\text{porp}$  = a porphyrin dianion,  $R$  = an aliphatic group, and  $L$  = amine) reveals that the nitroso ligand binds as an  $\eta^1-N(O)R$  moiety, while corresponding phthalocyanine derivatives with aromatic nitroso ligands were judged by NMR ring-current shift data (see below) to contain the same bonding mode [11].

Here we report on the isolation of  $Ru(\text{OEP})(\text{PhNO})_2$  (**1**) and  $Ru(\text{OEP})(\text{PhNO})\text{py}$ , and *in situ*

generation of  $Ru(\text{OEP})(\text{PhNO})L$  [where  $\text{OEP}$  = dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin,  $\text{py}$  = pyridine, and  $L$  = vacant,  $\text{CO}$ ,  $\text{H}_2\text{O}$ , or  $\text{PPh}_3$ ].

Treatment of 0.2 mmol of  $Ru(\text{OEP})(\text{CO})(\text{EtOH})$  [12] with 0.5 mmol  $\text{PhNO}$  in 150 ml  $\text{CH}_2\text{Cl}_2$  at  $\sim 20^\circ\text{C}$  under  $N_2$  rapidly yielded a solution containing the bis(nitrosobenzene) complex (**1**); removal of solvent by evaporation gave a purple powder, recrystallizable from boiling hexane (90%). *Anal. Calc.* for  $C_{48}H_{54}N_6O_2Ru$ : C, 67.98; H, 6.42; N, 9.91. *Found*: C, 67.82; H, 6.30; N, 9.90%. *Mass spec.*  $m/e$  1269  $[Ru(\text{OEP})]_2^+$ , 741  $Ru(\text{OEP})(\text{PhNO})^+$ , 634  $Ru(\text{OEP})^+$ , 107  $\text{PhNO}^+$ ;  $\nu\text{NO}$  1339  $\text{cm}^{-1}$  (Nujol);  $\lambda_{\text{max}}$  (nm) ( $\log \epsilon$  ( $M^{-1}\text{cm}^{-1}$ )) in  $\text{CH}_2\text{Cl}_2$ : 595(3.98), 531(4.28), 505(4.20), 392(5.10). NMR data for complex **1** are given in Table I, together with corresponding data for the other species studied. The porphyrin ring  $^1\text{H}$  resonances of **1** are typical of those for diamagnetic  $Ru(\text{II})$  species containing  $\text{OEP}$  [13, 14], while the equivalence of the methylene protons of the ethyl groups demonstrates mirror symmetry in the porphyrin plane for the solution structure [2, 13]. The upfield phenyl resonances of the coordinated  $\text{PhNO}$  result from the ring current exerted by the porphyrin, and the shifts for the *o*-, *m*- and *p*-protons are similar but somewhat greater (by about 1–2 ppm) than those observed for the corresponding bis(triphenylphosphine) [6] and bis(diphenylsulfide) [1] systems. For each type of proton, the upfield shifts decrease in the order  $\text{PhNO} > \text{Ph}_2\text{S} > \text{Ph}_3\text{P}$ ; crystallographic data on **1** will be needed to supplement those for  $Ru(\text{OEP})(\text{PPh}_3)_2$  [14] and  $Ru(\text{OEP})(\text{SPh}_2)_2$  [1], before any quantitative evaluation of this trend can be made. However, a strong IR band at 1339  $\text{cm}^{-1}$  is assignable to  $\nu(\text{NO})$  of  $\text{PhNO}$  bound via the nitrogen, on comparison with a structurally characterized  $Ru(\text{II})$  complex ( $\nu(\text{NO})$  1340  $\text{cm}^{-1}$ ) containing such a moiety [15]; for  $\eta^1-N(O)R$  ( $R$  = alkyl) at  $Fe(\text{II})$  porphyrin centres,  $\nu(\text{NO})$  is in the 1430  $\text{cm}^{-1}$  region [10].  $\eta^2$ -Bound nitroso ligands (side-on  $N-O$   $\pi$ -bond) reveal much lower  $\nu(\text{NO})$  values ( $\sim 1030 \text{cm}^{-1}$ ) [10, 16].

Binding through oxygen, which is possible [11, 16], is considered unlikely because the upfield shifts of the phenyl protons imply close proximity of these protons to the porphyrin plane. A  $Ru$ -axial  $N_{\text{sp}^2}$  bond length is typically 2.10–2.20 Å in (porphinato)-ruthenium(II) complexes [14], thus the  $Ru-S$  and  $Ru-P$  distances of 2.37 and 2.43 Å in  $Ru(\text{OEP})(\text{SPh}_2)_2$  [1] and  $Ru(\text{OEP})(\text{PPh}_3)_2$  [14], respectively, and the shift trend noted above, are consistent with the presence of a  $Ru-N$  bond in all the nitroso species listed in Table I.

The  $Ru(\text{OEP})(\text{PhNO})_2$  complex (**1**) is air-stable in the solid state and in solution. At NMR concentrations of  $10^{-3}$  M, only a single  $H_{\text{meso}}$  resonance is

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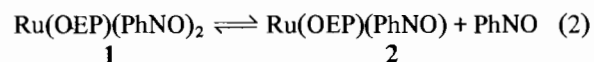
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TABLE I. NMR Data for some (Octaethylporphinato)ruthenium(II) Complexes<sup>a</sup>

Complex	H <sub>meso</sub>	CH <sub>2</sub>	CH <sub>3</sub>	H <sub>o</sub>	H <sub>m</sub>	H <sub>p</sub>
Ru(PhNO) <sub>2</sub> (1)	10.15s	3.96q	1.88t	2.25d	5.47t	5.86t
'Ru(PhNO)' (2) <sup>b</sup>	10.04s	3.99br	1.92t	2.35br	5.58br	5.93br
Ru(PhNO)py (3)	10.00s	3.94m	1.90t	2.53d (1.54d)	5.66t 4.05t	6.00t 4.59t <sup>c</sup>
Rupy <sub>2</sub> <sup>d</sup>	9.74s	3.97q	2.03t	2.26d	4.17m	4.33t
Ru(PhNO)(PPh <sub>3</sub> ) (4)	9.67s	3.85m	1.86t	2.20d (4.19m)	5.52t 6.33m	5.91t 6.54m <sup>e</sup>
Ru(PPh <sub>3</sub> ) <sub>2</sub> <sup>f</sup>	9.12s	3.75q	1.89t	4.36m	6.36t	6.57t
Ru(PhNO)(CO) (5) <sup>g</sup>	10.28s	3.93br	1.92t	2.29d	5.24t	5.65t
'Ru(CO)' (6) <sup>h</sup>	10.22s	3.94m	1.90t			
Ru(CO) <sub>2</sub>	10.24s	3.95q	1.90t			

<sup>a</sup>Ru implies Ru(OEP). Data measured on Varian XL-300 or Brücker WH-400 instruments at ~20 °C in C<sub>6</sub>D<sub>6</sub> unless stated otherwise. δ in ppm w.r.t. TMS; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. The integrations of the signals correspond in each case to the assignments given. <sup>b</sup>At -60 °C in toluene-d<sub>8</sub>. A variable intensity signal at δ -6.50s is attributed to coordinated trace water; at 20 °C this is replaced by a weak broader signal at δ -0.34, attributed to exchanging H<sub>2</sub>O (see text). <sup>c</sup>Signals of py. <sup>d</sup>Prepared according to a literature method [20]. <sup>e</sup>Signals of PPh<sub>3</sub>. <sup>f</sup>Taken from ref. 6. <sup>g</sup>At -60 °C. <sup>h</sup>At -60 °C, species formed *in situ* by dissolution of Ru(OEP)(CO)(EtOH) [14]; some coordinated H<sub>2</sub>O was detected at δ -6.94s, this being replaced at 20 °C by a broad signal at δ -0.66 (see footnote <sup>b</sup>).

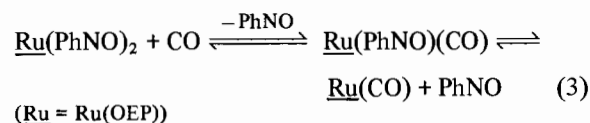
observed at 20 °C and this is unchanged in the presence of excess PhNO; similarly at 10<sup>-4</sup> M, the UV-Vis spectrum is independent of added nitroso ligand, implying that the equilibrium dissociation to give 2 according to eqn. (2) lies well to the left at these concentrations.



A sharpening of the proton resonances of bound PhNO within 1 at 0 °C provides some evidence for equilibrium (2). Further, 1 is labile in solution (see below), and the substitution reactions almost certainly proceed via a pre-dissociation such as (2) [2].

Treatment of CH<sub>2</sub>Cl<sub>2</sub> solutions of 1 with 2 mol equiv. of pyridine at 20 °C for 10 min allows for a quantitative yield of Ru(OEP)(PhNO)py (3) (Table I). *Anal. Calc.* for C<sub>47</sub>H<sub>54</sub>N<sub>6</sub>ORu: C, 68.78; H, 6.58; N, 10.24. Found: C, 68.40; H, 6.60; N, 10.19%. *Mass spectrometry*: *m/e* 1269 [Ru(OEP)]<sub>2</sub><sup>+</sup>, 741 Ru(OEP)(PhNO)<sup>+</sup>, 711 Ru(OEP)py<sup>+</sup>, 634 Ru(OEP)<sup>+</sup>, 107 PhNO<sup>+</sup>, 79 py<sup>+</sup>; ν(NO) 1329 cm<sup>-1</sup> (Nujol); λ<sub>max</sub> in CH<sub>2</sub>Cl<sub>2</sub>: 503(4.04), 480(4.03), 396(5.21). Complex 3 is formed also on treating Ru(OEP)py<sub>2</sub> [13] with excess PhNO, but the reaction takes days at ~20 °C, this reflecting the substitution inertness of the bis(pyridine) complex, *cf.* eqn. (2). The complex Ru(OEP)(PhNO)(PPh<sub>3</sub>) (4) is formed *in situ* from 1 and an equiv. of PPh<sub>3</sub> (λ<sub>max</sub> in CH<sub>2</sub>Cl<sub>2</sub>: 527(4.14), 508(4.11), 406(5.09); ν(NO) 1327 cm<sup>-1</sup>; Table I), but during attempted work-up procedures decomposition to several species, including Ru(OEP)(PPh<sub>3</sub>)<sub>2</sub>, occurred; 4 can be formed also via addition of 1.0 equiv. of PhNO to Ru(OEP)(PPh<sub>3</sub>)<sub>2</sub> [14] or Ru(OEP)(PPh<sub>3</sub>) [6].

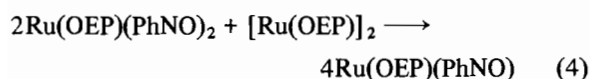
Subjecting CH<sub>2</sub>Cl<sub>2</sub> solutions of 1 to 1 atm CO (*cf.* reaction (1)) instantly gives the bis(carbonyl) Ru(OEP)(CO)<sub>2</sub> [17], but the mixed species Ru(OEP)(PhNO)(CO) (5) could be detected *in situ* at lower temperatures (<-40 °C) by addition of close to a stoichiometric amount of CO(g) to 1 via a syringe; free PhNO is also detected (δ 7.55, 6.75br) in such solutions, but the reaction does not yield 5 quantitatively, because H<sub>meso</sub> resonances of 1 and 'Ru(OEP)(CO)' (6) are seen also (Table I). Further, addition of 1 equiv. of PhNO to Ru(OEP)(CO)(EtOH) at 20 °C simply converted half of the carbonyl complex to 1. The <sup>1</sup>H NMR data indicate that the species involved in the equilibria outlined in eqn. (3) are highly labile:



The varying success in attempts to isolate the Ru(OEP)(PhNO)L complexes reveals a substitution character ranging from relatively inert (L = py), to labile (L = PPh<sub>3</sub>), to very labile (L = CO) and this mimics the reactivity trend for the corresponding Ru(OEP)(CO)L complexes [12, 14, 17]. These data certainly show the strong π-acid character for the nitroso ligand (as well as CO) in ruthenium porphyrins when *trans* to another π-acid, and the reactivity trends are consistent with the known π-acid strength of L (CO > PPh<sub>3</sub> > py). It is surprising that Ru(OEP)(PhNO)<sub>2</sub> at 10<sup>-4</sup>-10<sup>-3</sup> M does not dissociate measurably according to eqn. (2); the bis(carbonyl) and, to a less extent, the bis(triphenylphosphine) complex certainly do under corresponding

conditions [14, 17]. Dynamic *trans*-effects at octahedral metalloporphyrin centres are, however, strongly influenced by *cis*-effects of the N<sub>4</sub> macrocycle [18], and interaction between the phenyl protons of PhNO and the porphyrin may play a role.

In a search for the 5-coordinate species Ru(OEP)(PhNO) (2), complex **1** was mixed with [Ru(OEP)]<sub>2</sub> [13] in a mole ratio slightly greater than 2:1 at the  $\mu$ -mole level, eqn. (4), in an NMR tube containing toluene-d<sub>8</sub>, and variable temperature <sup>1</sup>H NMR studied (Table I). At -60 °C, a new H<sub>meso</sub> peak is seen at  $\delta$  10.04, and this and the associated resonances listed in Table I are attributed to a species containing a



single coordinated PhNO; the solutions typically contain about 10% of **1** whose <sup>1</sup>H resonances are still clearly discernible; at 20 °C, separate signals for both **1** and **2** are still observed, but at 40 °C averaged signals are observed, indicating exchange according to eqn. (2). A complication in this type of <sup>1</sup>H NMR study with five-coordinate metalloporphyrins (and noted by others [19]) is the presence of trace water in the toluene; a small <sup>1</sup>H NMR signal ( $\delta$  -6.50s) seen at -60 °C is attributed to coordinated H<sub>2</sub>O, while a broader signal seen at  $\delta$  -0.34 at 20 °C is considered to be an average exchange position between the bound and free H<sub>2</sub>O ( $\delta$  0.40). The water signals could be reduced to very low intensity with more rigorous drying treatment (activated Al<sub>2</sub>O<sub>3</sub> and molecular sieves), but were always present; the resonances of the 'five-coordinate' species (Table I) were essentially invariant with varying intensity of the H<sub>2</sub>O signals. The UV-Vis spectrum of Ru(OEP)(PhNO) formed *in situ* in rigorously dried CH<sub>2</sub>Cl<sub>2</sub> according to reaction (4) [ $\lambda_{\text{max}}$  (log  $\epsilon$ ): 590(3.80), 545(4.03), 498(4.19), 465(4.25), 390 nm (5.23)], is certainly different in type to that of the six-coordinate complexes **1**, **3** and **4**; an Fe(TPP)(<sup>1</sup>PrNO) complex [TPP = dianion of 5,10,15,20-tetraphenylporphyrin] has been isolated [10].

It should be noted that in species lacking a porphyrin mirror plane (2-6), the CH<sub>2</sub> protons of the ethyl groups become inequivalent (anisochronous) and the expected <sup>1</sup>H NMR ABX<sub>3</sub> pattern appears as a partly resolved multiplet [14].

In conclusion, we have shown that six-coordinate ruthenium(II) porphyrins containing one or two axially coordinated nitrosobenzenes ( $\eta^1$ -N(O)Ph) are readily synthesized; their substitution lability has been demonstrated, and evidence is presented for the five-coordinate species Ru(OEP)(PhNO) in solution. The stability of solutions of Ru(OEP)(PhNO)<sub>2</sub> (**1**)

towards air suggests that catalytic O<sub>2</sub>-oxidation of nitrosobenzene via **1** is unlikely, while the ready formation of Ru(OEP)(CO)<sub>2</sub> from **1** under 1 atm CO suggests that competitive ligand binding data (PhNO *versus* CO) are necessary before catalytic carbonylation systems can be tested for.

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