

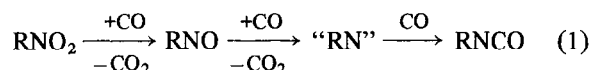
Nitrosobenzene Complexes of (Octaethylporphinato)-ruthenium(II)

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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 $Fe(porp)(RNO)L$ species (where $porp$ = 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 $Ru(OEP)(PhNO)_2$ (**1**) and $Ru(OEP)(PhNO)py$, and *in situ*

generation of $Ru(OEP)(PhNO)L$ [where OEP = dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin, py = pyridine, and L = vacant, CO , H_2O , or PPh_3].

Treatment of 0.2 mmol of $Ru(OEP)(CO)(EtOH)$ [12] with 0.5 mmol $PhNO$ in 150 ml CH_2Cl_2 at $\sim 20^\circ C$ 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 $[Ru(OEP)]_2^+$, 741 $Ru(OEP)(PhNO)^+$, 634 $Ru(OEP)^+$, 107 $PhNO^+$; νNO 1339 cm^{-1} (Nujol); λ_{max} (nm) ($\log \epsilon$ ($M^{-1}\text{ cm}^{-1}$))) in CH_2Cl_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 1H resonances of **1** are typical of those for diamagnetic $Ru(II)$ species containing 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 $PhNO$ 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 $PhNO > Ph_2S > Ph_3P$; crystallographic data on **1** will be needed to supplement those for $Ru(OEP)(PPh_3)_2$ [14] and $Ru(OEP)(SPh_2)_2$ [1], before any quantitative evaluation of this trend can be made. However, a strong IR band at 1339 cm^{-1} is assignable to $\nu(NO)$ of $PhNO$ bound via the nitrogen, on comparison with a structurally characterized $Ru(II)$ complex ($\nu(NO)$ 1340 cm^{-1}) containing such a moiety [15]; for $\eta^1-N(O)R$ (R = alkyl) at $Fe(II)$ porphyrin centres, $\nu(NO)$ is in the 1430 cm^{-1} region [10]. η^2 -Bound nitroso ligands (side-on $N-O$ π -bond) reveal much lower $\nu(NO)$ 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_{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 $Ru(OEP)(SPh_2)_2$ [1] and $Ru(OEP)(PPh_3)_2$ [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 $Ru(OEP)(PhNO)_2$ complex (**1**) is air-stable in the solid state and in solution. At NMR concentrations of 10^{-3} M , only a single H_{meso} resonance is

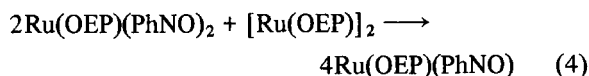
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The varying success in attempts to isolate the Ru(OEP)(PhNO)L complexes reveals a substitution character ranging from relatively inert (L = py), to labile (L = PPh₃), to very labile (L = CO) and this mimics the reactivity trend for the corresponding 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 > PPh₃ > py). It is surprising that Ru(OEP)(PhNO)₂ at 10⁻⁴–10⁻³ 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 N₄ 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)]₂ [13] in a mole ratio slightly greater than 2:1 at the μ -mole level, eqn. (4), in an NMR tube containing toluene-d₈, and variable temperature ¹H NMR studied (Table I). At -60 °C, a new H_{meso} peak is seen at δ 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 ¹H 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 ¹H NMR study with five-coordinate metalloporphyrins (and noted by others [19]) is the presence of trace water in the toluene; a small ¹H NMR signal (δ -6.50s) seen at -60 °C is attributed to coordinated H₂O, while a broader signal seen at δ -0.34 at 20 °C is considered to be an average exchange position between the bound and free H₂O (δ 0.40). The water signals could be reduced to very low intensity with more rigorous drying treatment (activated Al₂O₃ and molecular sieves), but were always present; the resonances of the 'five-coordinate' species (Table I) were essentially invariant with varying intensity of the H₂O signals. The UV-Vis spectrum of Ru(OEP)(PhNO) formed *in situ* in rigorously dried CH₂Cl₂ according to reaction (4) [λ_{max} (log ϵ): 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)(¹PrNO) 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 CH₂ protons of the ethyl groups become inequivalent (anisochronous) and the expected ¹H NMR ABX₃ 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 (η^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)₂ (1)

towards air suggests that catalytic O₂-oxidation of nitrosobenzene via 1 is unlikely, while the ready formation of Ru(OEP)(CO)₂ 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.

Acknowledgements

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