Nitrosobenzene Complexes of (Octaethylporphinato)ruthenium(II)

CORRADO CROTTI*, CHAND SISHTA,
ANDREW PACHECO and BRIAN R. JAMES**

Department of Chemistry, University of British Columbia, Vancouver, British Columbia V6T 1Y6, Canada

(Received June 1, 1987)

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]:

$$RNO_2 \xrightarrow[-CO_2]{+CO} RNO \xrightarrow[-CO_2]{+CO} \text{“RN”} \xrightarrow{CO} RNCO \qquad (1)$$

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 η^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 ~20 °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 ϵ (M^{-1} 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 ν(NO) of PhNO bound via the nitrogen, on comparison with a structurally characterized Ru(II) complex (ν(NO) 1340 cm^{-1}) containing such a moiety [15]; for η^1-N(O)R (R = alkyl) at Fe(II) porphyrin centres, ν(NO) is in the 1430 cm^{-1} region [10]. η^2-Bound nitroso ligands (side-on N–O π-bond) reveal much lower ν(NO) values (~1030 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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*On leave (1986) from Centro CNR Sintesi e Struttura, Via Venezian 21, 20133 Milan, Italy.

**Author to whom correspondence should be addressed.

0020-1693/88/$3.50

TABLE I. NMR Data for some (Octaethylporphinato)ruthenium(II) Complexes[a]

Complex	H_{meso}	CH_2	CH_3	H_o	H_m	H_p
$\underline{\text{Ru}}(\text{PhNO})_2$ (1)	10.15s	3.96q	1.88t	2.25d	5.47t	5.86t
'$\underline{\text{Ru}}(\text{PhNO})$' (2)[b]	10.04s	3.99br	1.92t	2.35br	5.58br	5.93br
$\underline{\text{Ru}}(\text{PhNO})\text{py}$ (3)	10.00s	3.94m	1.90t	2.53d	5.66t	6.00t
				(1.54d	4.05t	4.59t)[c]
$\underline{\text{Ru}}\text{py}_2$[d]	9.74s	3.97q	2.03t	2.26d	4.17m	4.33t
$\underline{\text{Ru}}(\text{PhNO})(\text{PPh}_3)$ (4)	9.67s	3.85m	1.86t	2.20d	5.52t	5.91t
				(4.19m	6.33m	6.54m)[e]
$\underline{\text{Ru}}(\text{PPh}_3)_2$[f]	9.12s	3.75q	1.89t	4.36m	6.36t	6.57t
$\underline{\text{Ru}}(\text{PhNO})(\text{CO})$ (5)[g]	10.28s	3.93br	1.92t	2.29d	5.24t	5.65t
'$\underline{\text{Ru}}(\text{CO})$' (6)[h]	10.22s	3.94m	1.90t			
$\underline{\text{Ru}}(\text{CO})_2$	10.24s	3.95q	1.90t			

[a] $\underline{\text{Ru}}$ implies Ru(OEP). Data measured on Varian XL-300 or Brücker WH-400 instruments at ~20 °C in C_6D_6 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. [b] At –60 °C in toluene-d_8. 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_2O (see text). [c] Signals of py. [d] Prepared according to a literature method [20]. [e] Signals of PPh_3. [f] Taken from ref. 6. [g] At –60 °C. [h] At –60 °C, species formed *in situ* by dissolution of Ru(OEP)(CO)(EtOH) [14]; some coordinated H_2O was detected at δ –6.94s, this being replaced at 20 °C by a broad singnal at δ –0.66 (see footnote [b]).

observed at 20 °C and this is unchanged in the presence of excess PhNO; similarly at 10^{-4} 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.

$$\underset{\mathbf{1}}{\mathrm{Ru(OEP)(PhNO)_2}} \rightleftharpoons \underset{\mathbf{2}}{\mathrm{Ru(OEP)(PhNO)}} + \mathrm{PhNO} \qquad (2)$$

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_2Cl_2 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 $C_{47}H_{54}N_6ORu$: C, 68.78; H, 6.58; N, 10.24. Found: C, 68.40; H, 6.60; N, 10.19%. *Mass spectrometry: m/e* 1269 $[\mathrm{Ru(OEP)}]_2^+$, 741 $\mathrm{Ru(OEP)(PhNO)}^+$, 711 $\mathrm{Ru(OEP)py}^+$, 634 $\mathrm{Ru(OEP)}^+$, 107 PhNO^+, 79 py^+; ν(NO) 1329 cm^{-1} (Nujol); λ_{max} in CH_2Cl_2: 503(4.04), 480(4.03), 396(5.21). Complex **3** is formed also on treating $\mathrm{Ru(OEP)py_2}$ [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 $\mathrm{Ru(OEP)(PhNO)(PPh_3)}$ (**4**) is formed *in situ* from **1** and an equiv. of PPh_3 (λ_{max} in CH_2Cl_2: 527(4.14), 508(4.11), 406(5.09); ν(NO) 1327 cm^{-1}; Table I), but during attempted work-up procedures decomposition to several species, including $\mathrm{Ru(OEP)(PPh_3)_2}$, occurred; **4** can be formed also via addition of 1.0 equiv. of PhNO to $\mathrm{Ru(OEP)(PPh_3)_2}$ [14] or $\mathrm{Ru(OEP)(PPh_3)}$ [6].

Subjecting CH_2Cl_2 solutions of **1** to 1 atm CO (*cf.* reaction (1)) instantly gives the bis(carbonyl) $\mathrm{Ru(OEP)(CO)_2}$ [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_{meso} 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 ^1H NMR data indicate that the species involved in the equilibria outlined in eqn. (3) are highly labile:

$$\underline{\mathrm{Ru}}(\mathrm{PhNO})_2 + \mathrm{CO} \overset{-\mathrm{PhNO}}{\rightleftharpoons} \underline{\mathrm{Ru}}(\mathrm{PhNO})(\mathrm{CO}) \rightleftharpoons \underline{\mathrm{Ru}}(\mathrm{CO}) + \mathrm{PhNO} \qquad (3)$$

($\underline{\mathrm{Ru}}$ = Ru(OEP))

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_3), 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_3 > py). It is surprising that $\mathrm{Ru(OEP)(PhNO)_2}$ 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 N_4 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-d_8, 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 H_2O, 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 H_2O (δ 0.40). The water signals could be reduced to very low intensity with more rigorous drying treatment (activated Al_2O_3 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_2O signals. The UV–Vis spectrum of Ru(OEP)(PhNO) formed *in situ* in rigorously dried CH_2Cl_2 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)(^{i}PrNO) complex [TPP = dianion of 5,10,15,20-tetraphenylporphyrin] has been isolated [10].

$$2Ru(OEP)(PhNO)_2 + [Ru(OEP)]_2 \longrightarrow 4Ru(OEP)(PhNO) \quad (4)$$

It should be noted that in species lacking a porphyrin mirror plane (**2**–**6**), the CH_2 protons of the ethyl groups become inequivalent (anisochronous) and the expected ^1H NMR ABX_3 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 O_2-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

We thank the Natural Sciences and Engineering Research Council of Canada for financial support, and Johnson Matthey Ltd. for the loan of ruthenium. One of us (C.C.) acknowledges support of a CNR grant.

References

1 B. R. James, A. Pacheco, S. J. Rettig, I. S. Thorburn, R. G. Ball and J. A. Ibers, *J. Mol. Catal., 41,* 147 (1987).

2 B. R. James, S. R. Mikkelsen, T. W. Leung, G. M. Williams and R. Wong, *Inorg. Chim. Acta, 85,* 209 (1984).

3 S. Cenini, M. Pizzotti and C. Crotti, in R. Ugo (ed.) 'Aspects of Homogeneous Catalysis', Vol. VI, Reidel, Dordrecht, in press.

4 *Eur. Pat. Appl., 4224* (1978) to J. M. Cognion and J. Kervennal; *Chem. Abstr., 92,* 41561 (1980).

5 G. W. Parshall, 'Homogeneous Catalysis', Wiley, New York, 1980, p. 93; A. F. M. Iqbal, *Chem. Technol.,* 566 (1974).

6 C. Sishta, M. J. Camenzind, B. R. James and D. Dolphin, *Inorg. Chem., 26,* 1181 (1987), and refs. therein.

7 M. D. Farnos, B. A. Woods and B. B. Wayland, *J. Am. Chem. Soc., 108,* 3659 (1986), and refs. therein.

8 J. T. Goves, in P. Ortiz de Montellano (ed.), 'Cytochrome P-450', Plenum, New York, 1985, Chap. I.

9 E. Antonini and M. Brunori, 'Hemoglobin and Myoglobin in Their Reactions with Ligands', North-Holland, Amsterdam, 1971.

10 D. Mansuy, P. Battioni, J.-C. Chottard, C. Riche and A. Chiaroni, *J. Am. Chem. Soc., 105,* 455 (1983).

11 J. J. Watkins and A. L. Balch, *Inorg, Chem., 14,* 2720 (1975).

12 M. Barley, J. Y. Becker, G. Domazetis, D. Dolphin and B. R. James, *Can. J. Chem., 61,* 2389 (1983).

13 J. P. Collman, C. E. Barnes, P. N. Swepston and J. A. Ibers, *J. Am. Chem. Soc., 106,* 3500 (1984).

14 S. Ariel, D. Dolphin, G. Domazetis, B. R. James, T. W. Leung, S. J. Rettig, J. Trotter and G. M. Williams, *Can. J. Chem., 62,* 755 (1984).

15 M. Pizzotti, C. Crotti and F. Demartin, *J. Chem. Soc., Dalton Trans.,* 735 (1984).

16 S. Otsuka, Y. Aotani, Y. Tatsuno and T. Yoshida, *Inorg. Chem., 15,* 656 (1976).

17 G. R. Eaton and S. S. Eaton, *J. Am. Chem. Soc., 97,* 235 (1975).

18 J. W. Buchler, W. Kokisch and P. D. Smith, *Struct. Bonding (Berlin), 34,* 79 (1978).

19 B. R. James, in D. Dolphin (ed.), 'The Porphyrins', Vol. V, Academic Press, New York, 1978, Chap. 6.

20 A. Antipas, J. W. Buchler, M. Gouterman and P. D. Smith, *J. Am. Chem. Soc., 100,* 3015 (1978).