Interaction between Dioxoruthenium(VI) Porphyrins and Hydroxylamines: Coordination of *N*-Substituted Hydroxylamine to Ruthenium and X-ray Crystal Structures of Ruthenium Complexes with a Unidentate Nitrosoarene Ligand

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Abstract: The interactions between dioxoruthenium(VI) porphyrins **1** with *N*-phenylhydroxylamine or unsubstituted hydroxylamine are described. Reaction of complexes **1** with excess PhNHOH leads to isolation of bis(nitrosobenzene)ruthenium(II) porphyrins **3** and mono(nitrosobenzene)ruthenium(II) porphyrins **4**. Both the types of ruthenium complexes are characterized by ^{1}H NMR, IR, and UV/Vis spectroscopy, and mass spectrometry. The X-ray structure determinations on [Ru^{II}(TPP)($PhNO)_2$] (**3a**), [Ru^{II}(2,6-Cl-TPP)($PhNO)_2$] (**3e**), and [Ru^{II}(4-MeO-TPP)(PhNO)($PhNH_2$)] (**4d**) (TPP = tetraarylporphyrin) disclose a unidentate nitrosoarene coordination in all these complexes, with Ru–N(PhNO) bond lengths of 2.003(3) (**3a**, average), 1.991(3) (**3e**, average), and 2.042(2) Å (**4d**). In the case of **4d**, the Ru–N($PhNH_2$) bond length is found to be 2.075(3) Å. Mechanistic investigations reveal the formation of intermediates [Ru^{II}(Por)(PhNO)(PhNHOH)] (**5**; Por = porphyrin), a ruthenium complex with *N*-substituted hydroxylamine ligand, in the "**1** + PhNHOH" system. The Ru–NH(OH)Ph moiety in **5** undergoes no rapid exchange with free PhNHOH in solution at room temperature, as revealed by ^{1}H NMR spectroscopy. Unlike the interaction between complexes **1** and PhNHOH, reaction of such complexes with NH_2OH affords nitrosylruthenium(II) porphyrins [Ru^{II}(Por)(NO)(OH)] (**6**).

Keywords: hydroxylamines · macrocyclic ligands · nitrosoarenes · ruthenium · structure elucidation

Introduction

Dioxoruthenium(VI) porphyrins, [$Ru^{VI}O_2$(Por)] (**1**; Por = porphyrin),[1, 2] exhibit a number of cytochrome P-450 type reactivities such as alkene epoxidation,[3–6] alkane hydroxylation,[7–9] and amine oxidation[10] (reactions (1) – (3) in Scheme 1), and serve as unique precursors to bis(amine)-,[11, 12] bis(imine)-,[13] bis(amido)-,[12, 14] bis(methyleneamido)-,[13] and bis(hydrazido)ruthenium porphyrins[15] (reactions (4) – (8) in Scheme 1). Our interest in the interaction between complexes **1** and hydroxylamines stems from the discovery that oxidative degradation of *N*-alkylhydroxylamines in the presence of cytochrome P-450 leads to formation of stable nitrosoalkane complexes of the enzyme,[16, 17] a reactivity well mimicked by the "[Fe^{III}(Por)Cl] + RNHOH (R = Me, *i*Pr, $PhCH_2CH_2$)" model systems developed by Mansuy and co-workers.[18, 19] Inasmuch as cytochrome P-450 also binds nitrosoarenes[20] and the oxidation processes catalyzed by this type of enzyme are widely believed to involve oxoiron porphyrin intermediates,[21] it would be of importance to examine the interaction between metalloporphyrin and *N*-arylhydroxylamine and, especially, to explore the reactivity of an oxometalloporphyrin toward various hydroxylamines. We notice that previous reports on the interaction between synthetic metalloporphyrins and hydroxylamines are extremely rare. Besides those on the foregoing "[Fe^{III}(Por)Cl] + RNHOH (R = Me, *i*Pr, $PhCH_2CH_2$)" systems, the only others are by Ryan and coworkers[22, 23] mainly on the reaction of [M^{III}(Por)Cl] (M = Fe, Mn) with NH_2OH to form nitrosyl metalloporphyrins. Conspicuously, no *oxometalloporphyrins* have been found to react with hydroxylamines to form nitroso or nitrosyl complexes.

On the other hand, the binding of nitrosoarene to synthetic metalloporphyrins has been demonstrated by James and coworkers[24] in the case of ruthenium octaethylporphyrin (OEP) and by Richter-Addo and co-workers[25] in the cases of iron,[26] manganese,[27] and osmium[28] *meso*-tetraarylpor-

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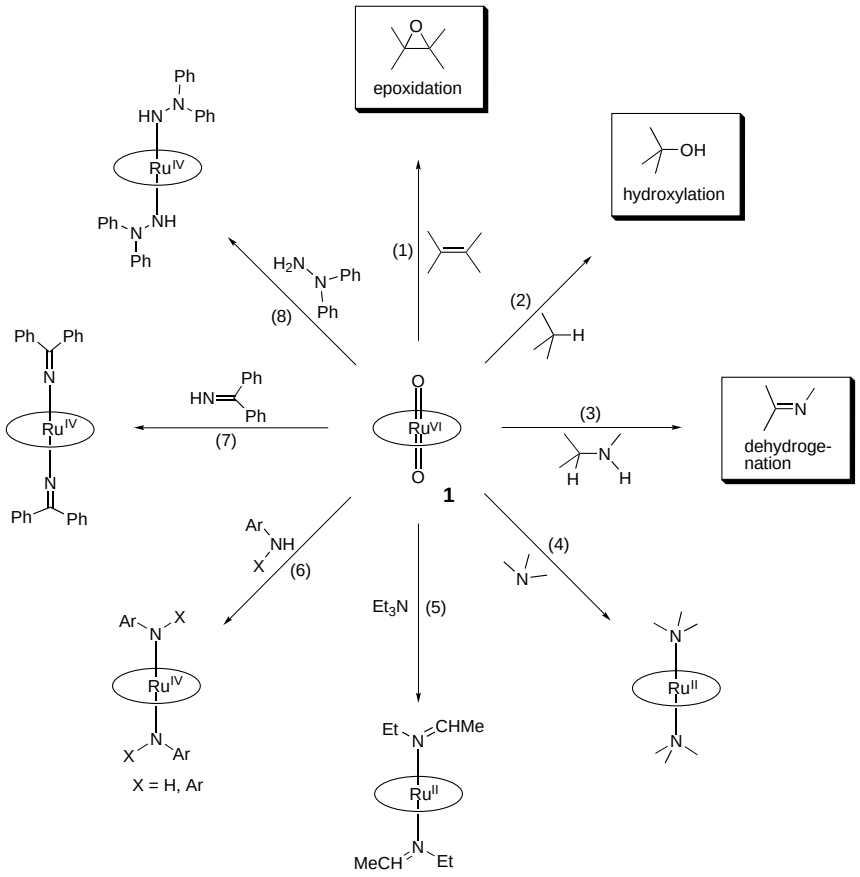
  0947-6539/01/0711-2306 $ 17.50+.50/0

phyrins.[29] The metalloporphyrin nitrosoarene complexes, $[M^{II}(Por)(ArNO)_2]$ and $[M^{II}(Por)(ArNO)(L)]$, in the above-mentioned studies are exclusively prepared *by direct reaction with nitrosoarenes* and are not structurally characterized in the case of ruthenium. Of all the structurally characterized metalloporphyrin nitrosoarene complexes,[25–28] only $[Os^{II}(TTP)(CO)(PhNO)]$ (**2**)[28] belongs to mono(nitrosoarene) complex, which bears a trans, *strongly* π*-acidic* carbonyl group. Since nitrosoarene groups are also strongly π-acidic ligands owing to their low-lying π* orbitals readily available for back-bonding,[19, 24, 28] a property that may result in considerable trans influence for both complexes $[M^{II}(Por)(ArNO)_2]$ and **2**,[30] it would be interesting to examine the structure of a $[M^{II}(Por)(ArNO)(L)]$ complex with L being a simple Lewis base, such as an amine; this will allow us to uncover the structural features of an M-ArNO moiety in metalloporphyrins uncomplicated by significant *trans* influence.



Scheme 1. Known reactivities of dioxoruthenium(VI) porphyrins (**1**) towards various organic compounds.

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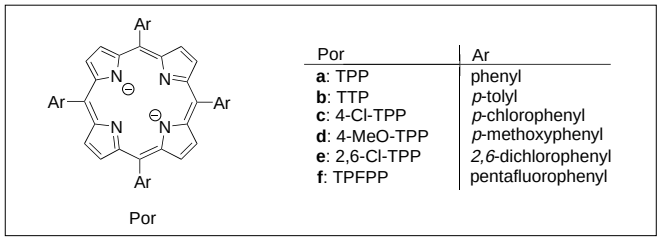
We report here the first investigation on the interaction between synthetic metalloporphyrin and *N*-arylhydroxylamine. The reaction of the dioxoruthenium(VI) complexes **1** with *N*-phenylhydroxylamine (PhNHOH) afforded stable nitrosoarene complexes $[Ru^{II}(Por)(PhNO)_2]$ (**3**) and $[Ru^{II}(Por)(PhNO)(NH_2Ph)]$ (**4**). Both the bis- and mono(nitrosobenzene) complexes have been characterized by X-ray crystallography, representing the first *structurally characterized* ruthenium complexes with a *unidentate* nitrosoarene ligand. Mechanistic studies on the "**1** + PhNHOH" system reveal the formation of intermediates $[Ru^{II}(Por)(PhNO)(PhNHOH)]$ (**5**), which to our knowledge constitute *the only ruthenium complexes binding an N-substituted hydroxylamine.* The reaction between complexes **1** and NH_2OH to afford nitrosylruthenium porphyrins $[Ru^{II}(Por)(NO)(OH)]$ (**6**) is also described.

Results and Discussion

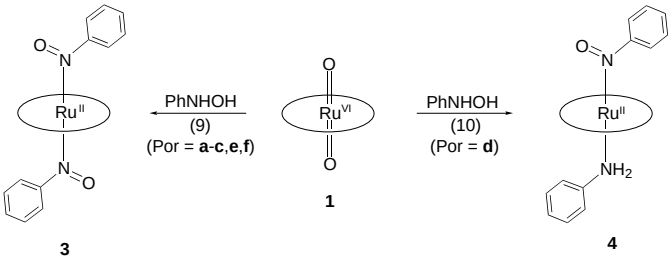
Reactions of dioxoruthenium(VI) porphyrins with *N*-arylhydroxylamine

*Isolation of complexes **3** and **4***: Mansuy and co-workers observed that reaction of $[Fe^{III}(Por)Cl]$ with excess *N*-alkylhydroxylamines forms iron-porphyrin *mono(nitrosoal-*

kane) complexes $[Fe^{II}(Por)(RNO)(L)]$ (R = *i*Pr, Me, $PhCH_2CH_2$) after addition of L (L = pyridine (Py), *i*$PrNH_2$, *N*-methylimidazole (*N*-MeIm), MeOH, $PPhMe_2$).[18, 19] If no L was added, only complex [Fe(TPP)(*i*PrNO)(*i*PrNHOH)] (**7**) (TPP = tetraarylporphyrin) was isolated.[19] Notably, none of these reactions were found to give bis(nitrosoalkane) complexes. In contrast, treatment of dioxoruthenium(VI) porphyrins **1a–c**, **1e**, and **1f** (Scheme 2) with an excess of the



Por	Ar
a: TPP	phenyl
b: TTP	*p*-tolyl
c: 4-Cl-TPP	*p*-chlorophenyl
d: 4-MeO-TPP	*p*-methoxyphenyl
e: 2,6-Cl-TPP	*2,6*-dichlorophenyl
f: TPFPP	pentafluorophenyl



Scheme 2. Isolation of complexes **3** and **4** from the interaction between complexes **1** and PhNHOH.

N-arylhydroxylamine PhNHOH in chloroform all led to the isolation of *bis(nitrosoarene)* complexes **3** after column chromatography on silica gel (reaction (9) in Scheme 2). The same procedure only gave the mono(nitrosoarene) complex **4d**, which unexpectedly binds aniline ($PhNH_2$)[31] rather than PhNHOH as an axial ligand, when complex **1d** was employed (reaction (10) in Scheme 2). To our surprise, the bis(nitrosoarene) analogue of **4d**, that is, [Ru(4-MeO-TPP)$(PhNO)_2$] (**3d**), could not be isolated according to this procedure despite several trials. We speculated that **3d** must be formed during the reaction, which can further react with the remaining PhNHOH to form **4d**. Indeed, ^{1}H NMR measurements on an in situ reaction between **1d** and two equivalents of PhNHOH in $CDCl_3$ reveal the formation of **3d** as the predominant porphyrin species (see Experimental Section). If a larger amount of PhNHOH (6 equiv) was used for the reaction, complex **4d** became the major porphyrin species, accompanied by the formation of free PhNO, $PhNH_2$, and azoxybenzene (PhN(O)=NPh) (see Experimental Section); the starting PhNHOH was completely consumed. This indicates that complex **1d** can *catalyze* the conversion of PhNHOH into PhNO, $PhNH_2$, and PhN(O)=NPh, which is in contrast to the stoichiometric reaction of $[Fe^{III}(Por)Cl]$ with RNHOH that consumes a maximum of 1.5 equivalents of RNHOH.[19]

The formation of both **3d** and **4d** in the in situ reaction of PhNHOH with **1d** suggests that similar phenomenon may also occur for the reaction of the same *N*-arylhydroxylamine with other dioxo complexes **1**. An in situ reaction between **1b** and PhNHOH (6 equiv) does form a mixture of **4b** and **3b** in ~2:1 molar ratio, as examined by ^{1}H NMR spectroscopy. However, attempts to isolate **4b** from the reaction mixture by column chromatography on silica gel were unsuccessful, the work-up of which gave complex **3b** as the only isolable product in 82% yield. Since the isolated yield of **3b** is markedly higher than that expected from the in situ reaction (~33%), it must be the case that **4b** is unstable toward the column chromatography and was partially changed into **3b** on the column of silica gel. This should also be true for the reaction of PhNHOH with complexes **1a**, **1c**, **1e**, and **1f**. Therefore, to isolate the **4d** analogues of other porphyrins, conditions that do not require column chromatography for product purification must be found. We eventually succeeded in isolating complex **4b** in 64% yield by addition of ethanol to the reaction mixture, which caused **4b** to precipitate from the solution without being contaminated by **3b**. In view of the instability of **4b** (and also its counterparts with other porphyrin ligands except 4-MeO-TPP) toward the column chromatography, it is puzzling why **4d** exhibits a remarkable stability during such a purification process.

A comparison of reactions (9) and (10) (Scheme 2) with reaction (6) (Scheme 1) reveals a dramatic difference between the interactions of **1** with *N*-arylhydroxylamine and arylamine. While bis(arylamido)ruthenium(IV) porphyrins can readily be prepared according to reaction (6),[12, 14] no bis(*N*-arylhydroxylamido)ruthenium(IV) porphyrins were isolated from the "**1** + PhNHOH" system. Furthermore, we have demonstrated the feasibility of isolating a bis(arylamine)ruthenium(II) porphyrin from reaction (4) (Scheme 1);[12] however, none of bis(*N*-phenylhydroxylamine)ruthenium(II) porphyrins were observed even in the in situ reactions between complexes **1** and excess PhNHOH.

Spectral features of complexes 3 and 4: Complexes **3** and **4** all exhibit diamagnetic ^{1}H NMR spectra. The spectral data are summarized in Table 1. Figure 1 shows the spectra of **3b** and **4b** as an example. In both spectra shown in Figure 1, only a sharp H_β signal appears, with the shapes and chemical shifts of all signals virtually unaffected by addition of PhNO (**3b**) or $PhNH_2$ (**4b**). This indicates that there is no detectable dissociation of the complexes in solution under the ^{1}H NMR conditions ([complex] ~10^{-2} M), as in the case of the OEP complex $[Ru(OEP)(PhNO)_2]$ (**8**).[24] As expected for the symmetrical axial coordination of **3b**, only one set of H_o, H_m, H_o(ax), H_m(ax), and H_p(ax) signals appears in Figure 1a. In contrast, two sets of H_o(ax), H_m(ax), and H_p(ax) signals with equal intensity are clearly observed in Figure 1b, and the H_o and H_m signals both appear as a multiplet rather than a doublet, consistent with the unsymmetrical axial coordination of **4b**. The NH_2 signal of the coordinated $PhNH_2$ in **4b**, which disappears upon addition of D_2O, is located at the highest field ($\delta = -2.80$). In view of the increase of H_β chemical shift with the increase in the oxidation state of the metal in diamagnetic metalloporphyrins[12, 13] and, hence, with the decrease of the electron density of the porphyrin macrocycle, the observed smaller H_β chemical shift of **4b** ($\delta = 8.42$) than that of **3b** ($\delta = 8.55$) is not unexpected considering the strong π-acid charac-

0947-6539/01/0711-2308 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 11

Table 1. ^{1}H NMR spectral data (δ, $CDCl_3$) of complexes **3**–**5**.[a]

	H_β (s, 8H)	H_o, H_o' (8H)	H_m, H_m' (8H)	*p*-X[b]	Axial ligand			
					H_p(ax), H_p(ax)′ (t, 1H), (t, 1H)	H_m(ax), H_m(ax)′ (t, 2H), (t, 2H)	H_o(ax), H_o(ax)′ (d, 2H), (d, 2H)	Others[c]
3a	8.54	8.12 (m)	7.73 (m)[d]		6.48	6.00	2.42	
3b	8.55	8.01 (d)	7.52 (d)	2.69	6.45	5.97	2.39	
3c	8.53	8.04 (d)	7.71 (d)		6.48	5.98	2.36	
3d	8.57	8.03 (d)	7.25 (d)	4.09	6.45	5.97	2.39	
3e	8.37		7.72 (m)[d]		6.35	5.92	2.92	
3f	8.55				6.46	5.97	2.52	
4a[e]	8.42	8.06 (m)	7.73 (m)[d]		6.43, 6.31	6.02, 5.98	2.67, 2.54	−2.68
4b	8.42	7.91 (m)	7.49 (m)	2.68	6.35, 6.27	5.98, 5.91	2.62, 2.52	−2.80
4d	8.44	7.95 (m)	7.21 (m)	4.07	6.36, 6.28	5.98, 5.91	2.61, 2.52	−2.78
4f	8.42				6.34, 6.20	5.95, 5.91	2.72, 2.63	−3.05
5a[e]	8.49	8.06 (m)	7.74 (m)[d]		6.47, 6.44	6.13, 5.97	2.92, 2.42	0.40, −1.09
5b	8.49	7.93 (m)	7.51 (m)	2.68	6.41, 6.35	6.07, 5.89	2.86, 2.41	0.34, −1.05
5d	8.50	7.96 (m)	7.28 (m)	4.09	6.42, 6.36	6.07, 5.89	2.86, 2.39	0.28, −1.06
5f	8.49				6.34, 6.34	6.06, 5.89	2.97, 2.50	0.08, −1.31

[a] For complexes **3**, H_o, H_p, H_p(ax), H_m(ax), and H_o(ax) are identical to H_o', H_p', H_p(ax)′, H_m(ax)′, and H_o(ax)′, respectively. [b] **3a**, **3e**, **4a**, **5a**: X = H; **3b**, **4b**, **5b**: X = Me (s, 12H); **3d**, **4d**, **5d**: X = OMe (s, 12H). [c] NH_2 (s, 2H) for **4a**, **4b**, **4d**, **4f**; NH (s, 1H) and OH (s, 1H) for **5a**, **5b**, **5d**, **5f**. All these signals disappeared after addition of D_2O. [d] H_m, H_m', H_p (12H). [e] In CD_2Cl_2.

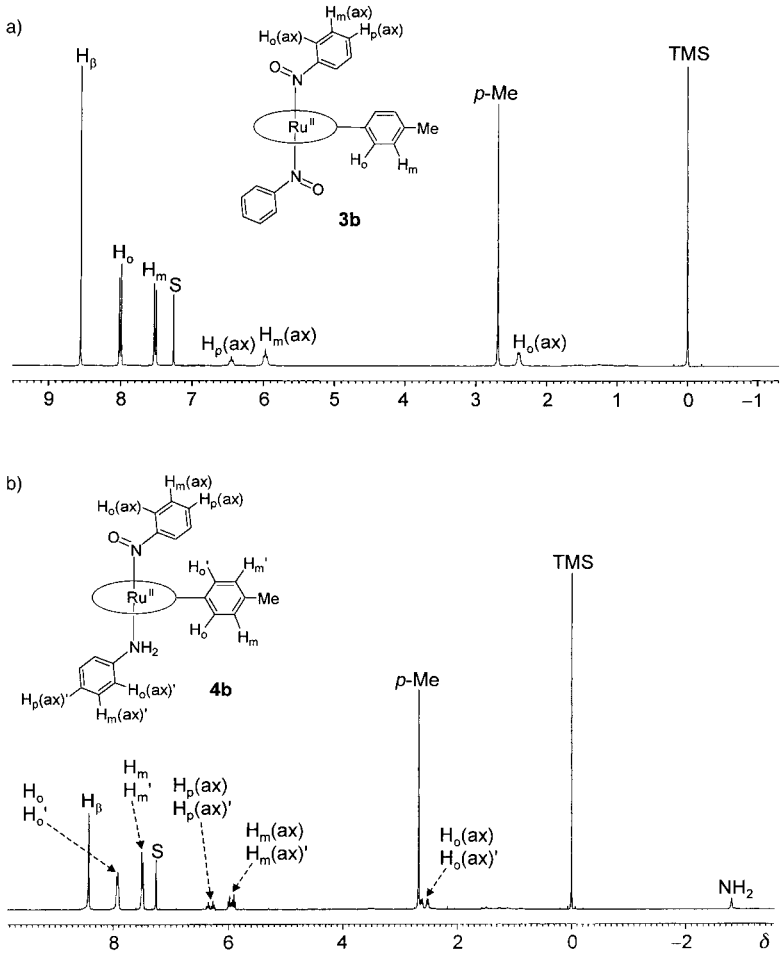


Figure 1. ^{1}H NMR spectra of a) complex **3b** and b) complex **4b** in $CDCl_3$.

ter of PhNO and the simple Lewis base character of $PhNH_2$. Examination of Table 1 reveals that the chemical shifts of H_β protons or the protons in the axial ligands for complexes **3** or **4** with porphyrin macrocycles **a**–**d** (see Scheme 2) are very similar, indicating that the influence of the *para*-substituents Me, Cl, MeO (on the *meso*-phenyl groups of the porphyrin ring) on these proton resonances is negligible. However, such chemical shifts for the complexes with porphyrin macrocycles **e** and **f** (especially the former) are appreciably different. In all cases, the signals of axial PhNO ligand appear at considerably lower fields in **3a**–**f** than in their OEP counterpart **8**, in agreement with the smaller porphyrin-ring-current effect expected for *meso*-tetraarylporphyrins than for OEP. A comparison of the H_β chemical shifts of **3** and **4** with those of respective carbonyl, bis(amine)-, and bis(imine) analogues does reveal that the PhNO ligand has a strong π acidity. For example, the H_β chemical shifts observed for **3b** and **4b** are substantially larger than that of $[Ru^{II}(TTP)(L)_2]$ (L = $NHEt_2$: $\delta = 8.08$, L = N(Et)=CHMe: $\delta = 8.09$)[13] although smaller than that of $[Ru^{II}(TTP)(CO)(MeOH)]$[4] ($\delta = 8.69$).

The IR spectra of **3** and **4** show "oxidation-state marker" bands[12, 13] ranging from 1006–1013 cm^{-1}, with their dependence on the substituents on the *meso*-phenyl rings of the porphyrin macrocycles similar to the case of H_β chemical shifts described above. A comparison of the "oxidation-state marker" bands of **3** and **4** with those of respective carbonyl,

bis(amine)-, and bis(imine) analogues discloses a trend basically parallel to that observed in terms of the H_β chemical shifts of these ruthenium porphyrins. For example, the "oxidation-state marker" band is found to be 1011 cm^{-1} for **3b**, 1008 cm^{-1} for **4b**, 1008 cm^{-1} for $[Ru^{II}(TTP)(CO)(MeOH)]$, and ~999 cm^{-1} for $[Ru^{II}(TTP)(L)_2]$ ($L = NHEt_2$ or N(Et)=CHMe).[13] James and co-workers reported that a strong band at 1339 cm^{-1} in the IR spectrum of **8** is assignable to the ν(NO) of the coordinated PhNO.[24] In our case, the intense bands of the *meso*-tetraarylporphyrin ligands in the region of interest preclude the identification of such ν(NO) bands for either **3** or **4**.

The UV/Vis spectra of bis(nitrosobenzene) complexes **3a–c** feature bands at ~410 (Soret) and ~515 nm (β), neither of which is appreciably changed upon addition of free PhNO. In comparison, the mono(nitrosobenzene) complexes **4b** and **4d** have considerably red-shifted β bands (~535 nm), although their Soret bands are similar to those of **3b** and **3d**. Again, such bands of **4b** and **4d** are virtually unaffected upon addition of free $PhNH_2$. Note that the UV/Vis spectra of **3e** (β band: 530 nm) and **3f** (β band: 533 nm) are significantly different from those of **3a–c**, but rather similar to those of **4b** and **4d**, possibly suggesting a considerable dissociation of **3e** and **3f** in the dilute solutions ([complex] = ~10^{-5} M). We did observe that the β bands of **3e** and **3f** in the presence of free PhNO (~520 nm) became closer to those of **3a–c**.

In the mass spectra of either **3** or **4**, the most intense peaks usually correspond to the fragments $[Ru(Por)(PhNO)]^+$, like the cases of previously reported metalloporphyrin nitrosoalkane[19] or nitrosoarene complexes.[24, 28] In some cases (such as **3b**, **3f**, **4b**, and **4d**) the peaks assignable to the parent ions are observed, but their intensities are rather weak.

*X-ray crystal structure determinations of complexes **3a**, **3e**·CH_2Cl_2·$CHCl_3$, and **4d**·2$CHCl_3$*: It has been well documented that nitrosoarene or -alkane ligands exhibit a variety of coordination modes, the most common of which is the unidentate N-coordination M–N(O)X (X = R or Ar).[32] To unambiguously ascertain the coordination modes of the nitrosobenzene ligand in the bis- and mono(nitrosoarene) complexes **3** and **4**, we determined the structures of both types of ruthenium porphyrin complexes by X-ray crystallography using single crystals of **3a**, **3e**·CH_2Cl_2·$CHCl_3$, and **4d**·2$CHCl_3$. The corresponding crystal and structure refinement data are given in Table 2. Figures 2–4 depict the ORTEP drawings of these complexes together with the atomic numbering schemes (hydrogen atoms and solvent molecules, if any, are omitted for clarity). Selected bond lengths and angles are listed in Table 3. Evidently, all the three complexes isolated from the "**1** + PhNHOH" system bear a unidentate, N-coordinating, nitrosobenzene ligand.[33] Prior to this work, quite a few ruthenium complexes with nitrosoalkane or -arene ligands were reported,[24, 34–43] but in none of the structurally characterized ones does a nitrosoarene ligand adopt the unidentate coordination.[44]

The structures of **3a**, **3e**, and **4d** all contain a distorted octahedral RuN_6 coordination core, whose axial N-Ru-N angle and *average* Ru–N(Por) bond length lie in the range of 171.6(1)–178.9(1)° and 2.048(2)–2.051(3) Å, respectively (Table 3). The porphyrin ring in each of these complexes is virtually planar, with its 24 omponent atoms showing a mean deviation of 0.0382 (**3a**)/0.0306 (**3e**)/0.0356 Å (**4d**) from the least-squares plane. The orientations of the axial ligands with respect to the porphyrin ring planes are depicted in Figure 5. For all the three complexes, the axial Ru-N(O)-C moiety

Table 2. Crystal data and structure refinement for complexes **3a**, **3e**, and **4d**.

	3a	**3e**·CH_2Cl_2·$CHCl_3$	**4d**·2$CHCl_3$
formula	$C_{56}H_{38}N_6O_2Ru$	$C_{56}H_{30}Cl_8N_6O_2Ru \cdot CH_2Cl_2 \cdot CHCl_3$	$C_{60}H_{48}N_6O_5Ru \cdot 2CHCl_3$
M_R	928.03	1407.82	1272.85
λ [Å]	0.71073	0.71073	0.71073
T [K]	301	294	294
crystal system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	Cc	$P1$
a [Å]	11.314(3)	12.098(2)	11.418(1)
b [Å]	11.513(4)	42.254(5)	11.419(1)
c [Å]	18.301(4)	12.309(2)	11.496(1)
α [°]	82.32(2)	90	94.021(2)
β [°]	77.94(2)	115.076(2)	100.172(2)
γ [°]	73.05(2)	90	97.613(2)
V [Å^3]	2223(1)	5699(1)	1455.5(2)
Z	2	4	1
ρ_{calcd} [Mg m^{-3}]	1.386	1.641	1.452
μ ($Mo_{K\alpha}$) [mm^{-1}]	0.404	0.94	0.600
F(000)	952	2816	650
index ranges	$-12 \le h \le 13$	$-14 \le h \le 15$	$-11 \le h \le 14$
	$0 \le k \le 13$	$-48 \le k \le 54$	$-14 \le k \le 14$
	$-21 \le l \le 21$	$-16 \le l \le 10$	$-14 \le l \le 14$
reflections collected	8263	19044	9751
independent reflections	7838	9467	7869
parameters	586	755	740
goodness-of-fit	1.64	0.888	1.131
final R indices [$I > 2\sigma(I)$]	$R^{[a]} = 0.035$, $wR^{[a]} = 0.044$	$R1 = 0.0573$, $wR2 = 0.1372$	$R1 = 0.064$, $wR2 = 0.169$
largest difference peak/hole [e Å^{-3}]	1.04/−0.56	0.921/−0.905	0.929/−0.711

[a] $I > 3\sigma(I)$.

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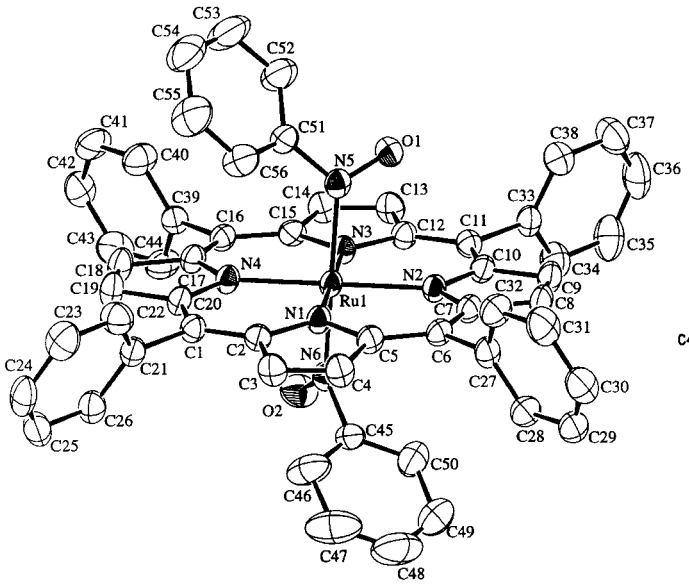


Figure 2. ORTEP drawing and the atomic numbering scheme for complex **3a** with thermal ellipsoids on the 40% probability level.

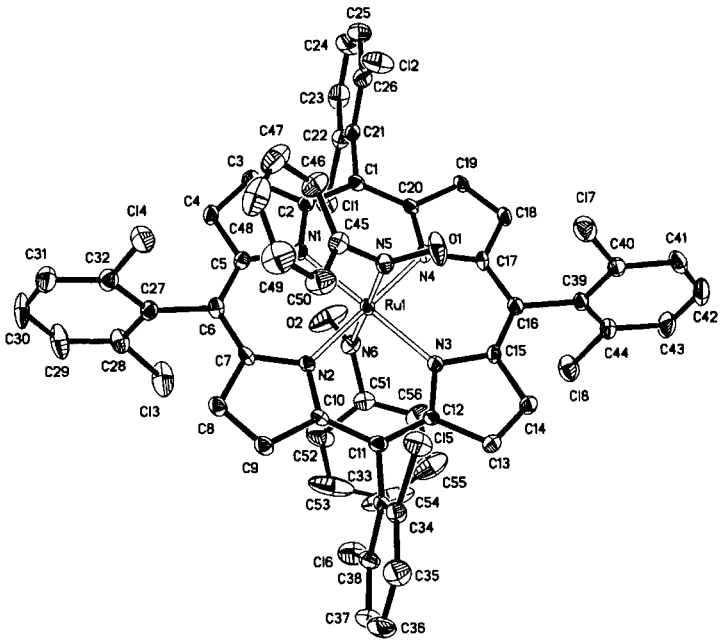


Figure 3. ORTEP drawing and the atomic numbering scheme for complex **3e** with thermal ellipsoids on the 50% probability level.

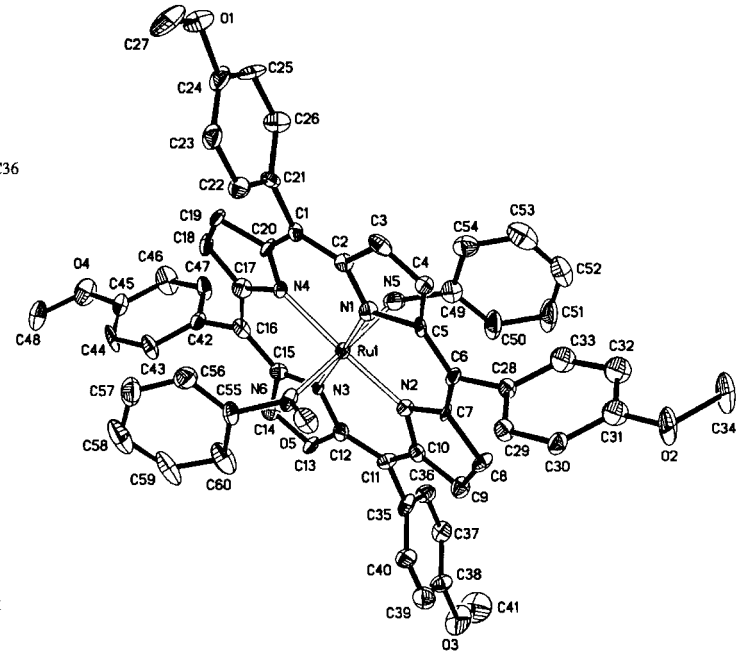


Figure 4. ORTEP drawing and the atomic numbering scheme for complex **4d** with thermal ellipsoids on the 50% probability level.

Table 3. Selected bond lengths [Å] and angles [°] for complexes **3a**, **3e**, and **4d**.

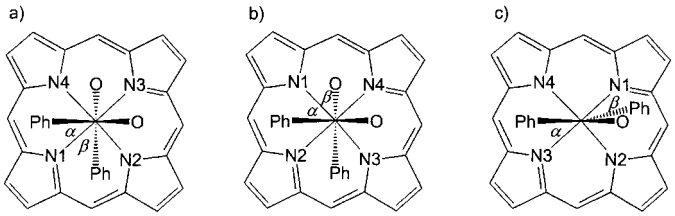
	3a	**3e**	**4d**
Ru1–N1	2.055(3)	2.051(2)	2.013(2)
Ru1–N2	2.052(3)	2.061(2)	2.014(2)
Ru1–N3	2.047(3)	2.043(2)	2.077(2)
Ru1–N4	2.050(3)	2.038(2)	2.087(2)
Ru1–N5	2.052(3)	1.967(2)	2.075(3)
Ru1–N6	1.954(3)	2.014(3)	2.042(2)
N5–O1	1.241(3)	1.235(3)	
N6–O2[a]	1.235(3)	1.236(4)	1.159(3)
N1-Ru1-N2	89.6(1)	89.58(9)	88.10(8)
N2-Ru1-N3	90.2(1)	89.96(9)	90.55(8)
N3-Ru1-N4	90.2(1)	90.27(9)	90.88(8)
N4-Ru1-N1	89.9(1)	90.18(9)	90.43(8)
N5-Ru1-N6	171.6(1)	177.39(9)	178.9(1)
Ru1-N5-C51[b]	127.7(2)	125.2(2)	122.3(2)
Ru1-N5-O1	117.6(2)	122.0(2)	
Ru1-N6-C45[c]	124.0(2)	127.1(2)	118.9(2)
Ru1-N6-O2[a]	123.7(2)	121.6(2)	118.6(2)
O1-N5-C51[b]	113.2(3)	112.8(3)	
O2[a]-N6-C45[c]	112.3(3)	111.2(3)	122.5(2)

[a] O5 for **4d**. [b] C45 for **3e**; C49 for **4d**. [c] C51 for **3e**; C55 for **4d**.

exhibits an excellent planarity (the sum of the component bond angles ranges from 358.5-360°), consistent with the sp^2 nature of the nitrosobenzene N atom.

In the case of the bis(nitrosoarene) complexes, the average Ru–N(PhNO) bond lengths (**3a**: 2.003(3), **3e**: 1.991(3) Å) are appreciably larger than the Ru–N(EtNO) bond length of 1.918(2) Å in the organometallic nitrosoalkane complex [(η^5-C_5Me_5)Ru(EtNO)(Ph)($PPhMe_2$)],[38] but smaller than the corresponding bond lengths of 2.093(4) – 2.115(7) Å in ruthenium complexes with η^2-nitrosoarene ligands.[40, 42, 43] The two axial PhNO ligands in either **3a** or **3e** adopt a staggered conformation, as can be seen from Figure 5. Such a conformation is considered beneficial to the axial M → N(O)Ar back-bonding in [M(Por)($ArNO)_2$], such as the osmium analogues of **3**.[28] The dihedral angles between the two Ru-N(O)-C least-squares planes are determined to be 84.4 (**3a**) and 70.4° (**3e**).

Compared with the structures of **3a** and **3e**, the mono-(nitrosoarene) complex **4d** has a substantially larger C-N-O angle, but smaller Ru-N-C and Ru-N-O angles for the Ru–N(O)Ph moiety (Table 3); this indicates that the PhNO ligand in **4d** is more "open" and may have a greater delocalization over the N=O and the attached phenyl



3a: $\alpha = 62.3°$, $\beta = 33.7°$ **3e**: $\alpha = 46.8°$, $\beta = 23.7°$ **4d**: $\alpha = 42.6°$, $\beta = 44.6°$

Figure 5. Orientations of the axial ligands with respect to the porphyrin ring for a) complex **3a**, b) complex **3e**, and c) complex **4d**.

groups.[45] The larger difference between the Ru–N1 (or Ru–N2) and Ru–N3 (or Ru–N4) bond lengths in **4d** than in **3a** and **3e** shows that the ruthenium atom in **4d** is more greatly displaced from the center of the equatorial RuN_4 plane.

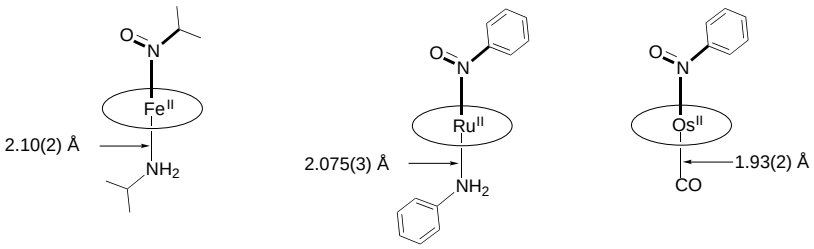
Strikingly, although the Ru–N(O)Ph bonding in **4d** may benefit from a push-pull effect in view of the π-acid character of PhNO and the Lewis base character of $PhNH_2$, this mono(nitrosoarene) complex has a *rather long* Ru–N(PhNO) bond (2.042(2) Å), which is even longer than the corresponding bonds in the bis(nitrosoarene) complexes **3a** and **3e**, and a *short* N–O bond (1.159(3) Å), which is even shorter than that reported for free PhNO (1.17 – 1.24 Å);[46] this is very different from the observations on a mono(nitrosoalkane) analogue of **4d**, that is, $[Fe^{II}(TPP)(i\text{PrNO})(i\text{PrNH}_2)]$ (**9**),[19] which features a fairly short Fe–N(*i*PrNO) bond (1.86 Å) with the N–O bond appreciably longer than that assumed for a free nitrosoalkane. Apparently, despite the strong π-acid character of the PhNO ligand, there is no considerable *trans* influence in the bis(nitrosoarene) complexes **3**, in contrast to the case of the osmium complex **2**, which bears mixed axial ligands CO/PhNO.[28, 30] Another notable feature in the structure of **4d** is the rather short Ru–N($PhNH_2$) bond of 2.075(3) Å, which is ~0.12 Å shorter than the Ru–N(L) bond in $[Ru^{II}(TPP)(CO)(L)]$ (L = Py or 1-MeIm).[47] This is surprising in view of the weaker Lewis basicity of aniline than pyridine and imidazole. Since no other ruthenium porphyrins with an axial arylamine ligand have been structurally characterized, it remains unclear whether the trans Ru–N(O)Ph group is responsible for the short Ru–N($PhNH_2$) bond in **4d**.

Table 4 shows a comparison of the M–N(O)X moieties among the three structurally characterized metalloporphyrin mono(nitrosoalkane or -arene) complexes **2**, **4d**, and **9**. In spite of the above-mentioned unusual structural features of **4d**, the trend of the M–N(XNO) bond length: **9** < **4d** < **2** is consistent with the Lewis basicity $i\text{PrNH}_2 > \text{PhNH}_2$ and the strong π-acid character of CO;[48] the larger C-N-O angles of the nitrosoarene complexes **2** and **4d** than that of the nitrosoalkane complex **9** are in agreement with the structure features of nitrosoarene and nitrosoalkane.[45] Of particular interest is the large difference (~0.21 Å) between the M–N(XNO) and M–C(CO) bond lengths in **4d** and $[Ru^{II}(TPP)(CO)(L)]$ (L = Py or 1-MeIm)[47] compared with the corresponding difference (~0.07 Å) in **9** and $[Fe^{II}(TPP)(CO)(L)]$ (L = Py or 1-MeIm).[47] This probably suggests either a considerably weaker M–N(O)Ar bonding than M–N(O)R[49] or a remarkable sensitivity of the M–N(O)Ar bonding to the basicity of the trans ligand L in $[M^{II}(Por)(XNO)(L)]$ complexes.

Mechanistic aspects: Despite the importance of the interaction between metalloporphyrin and *N*-substituted hydroxylamines, the mechanism of such interaction has not been investigated in a considerable detail. To account for the observed stoichiometry for the two-electron oxidation of RNHOH to RNO under anaerobic conditions in the "$[Fe^{III}(Por)Cl]$ + RNHOH" system, Mansuy and co-workers proposed that both the reactants serve as a one-electron oxidant.[19] However, in the "**1** + PhNHOH" system, the formation of ruthenium(II) complexes **3** and **4** indicates a four-electron oxidant nature of the ruthenium(VI) complexes **1**. This feature, together with the catalytic formation of PhN(O)=NPh and $PhNH_2$, signifies the operation of a more complicated mechanism in the interaction between **1** and PhNHOH.

Inasmuch as complexes **1** are prone to undergo oxygen atom transfer reactions,[3–9] a mechanism as shown in Scheme 3 reaction (11) seems probable; this is analogous to that reported for the oxidation of ArNHOH with methylrhenium trioxide.[50] However, reaction (11) alone requires only two equivalents of PhNHOH to reach completion and can account for neither the formation of complexes **4** nor the catalytic production of $PhNH_2$ in the system. Recognizing that complexes **3** formed from reaction (11) are reactive to hydroxylamine (vide supra), it is likely that these complexes can catalyze the disproportionation of PhNHOH to form PhNO and $PhNH_2$.[51] To provide support for this, we examined the reac-

Table 4. Comparison of the structural features of M–N(O)R or M–N(O)Ar moieties in metalloporphyrins with mononitrosoalkane or -arene axial ligands.



	9[a]	**4d**	**2**[b]
M–N	1.86(1)	2.042(2)	2.18(2)
N–O	1.26(2)	1.159(3)	1.26(2)
N–C	1.55(2)	1.434(3)	1.39(3)
M-N-O	124(1)	118.6(2)	113(2)
M-N-C	119(1)	118.9(2)	122(1)
C-N-O	117(1)	122.5(2)	120(2)

[a] Ref. [19]. [b] Ref. [28].

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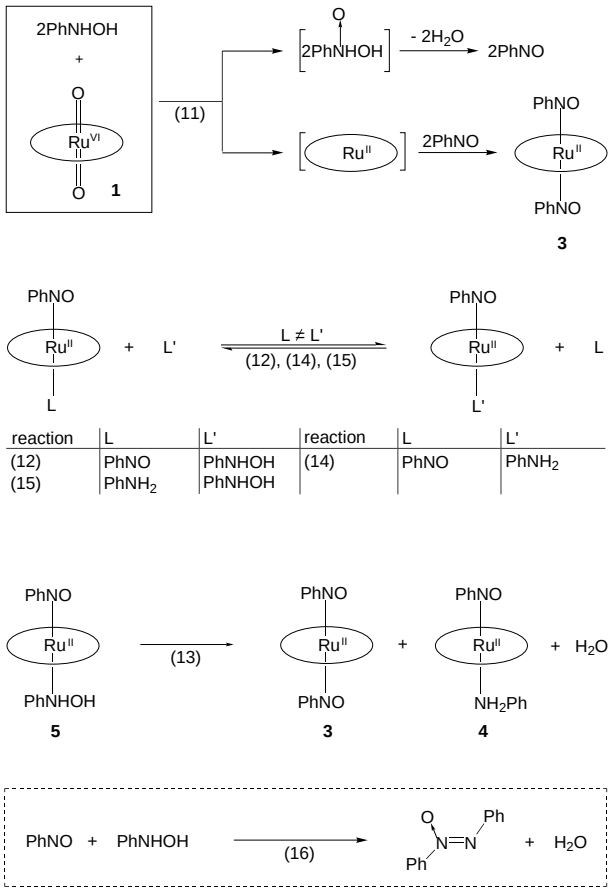


Scheme 3. Proposed mechanism for the interaction between complexes **1** and *N*-phenylhydroxylamine.

tivity of the isolated **3** toward PhNHOH. When **3a** was treated with four equivalents of PhNHOH in CD_2Cl_2, a new complex was formed almost quantitatively within ten minutes, whose ^{1}H NMR spectrum (Figure 6a and Table 1) is entirely consistent with the formulation [Ru^{II}(TPP)(PhNO)(PhNHOH)] (**5a**).[52] Integration of the signals in Figure 6a gives an expected **5a**:PhNHOH(free):PhNO(free) molar ratio of ~1:3:1, indicating the occurrence of reaction (12) in Scheme 3. After the reaction mixture was kept for two hours, **5a** almost completely disappeared (Figure 6b), with concomitant formation of **3a** and **4a** in ~1:8 molar ratio (reaction (13) in Scheme 3).[53] At this stage, no PhNHOH was detected, and the organic products observed are PhN(O)=NPh, PhNO, and $PhNH_2$ (molar ratio: ~1:1.5:1). Similar phenomena were also observed for **3b** and **3f**. To further examine the catalytic behavior of **3** toward the PhNHOH disproportionation, we treated the hydroxylamine with 2 mol% of **3f** under an inert atmosphere; this resulted in a ~50% substrate conversion within three days. The organic products formed in this case are PhN(O)=NPh and $PhNH_2$; no PhNO was observed (see Experimental Section).

In view of the weaker basicity of PhNHOH than $PhNH_2$,[52] the facile formation of **5** from **3** suggests that **3** would also react with $PhNH_2$ to form **4**. Indeed, treatment of **3b** or **3f** with six equivalents of $PhNH_2$ in $CDCl_3$ gave rise to **4b** or **4f** as the only detectable porphyrin species (reaction (14) in Scheme 3). Worthy of note is that reaction (14) is reversible. When the isolated **4d** was treated with four equivalents of PhNO in $CDCl_3$, about half of the amount of the complex was converted into **3d**. This indicates the presence of an equilibrium among **3**, **4**, PhNO, and $PhNH_2$. Interestingly, although $PhNH_2$ is more strongly basic than PhNHOH, the bound $PhNH_2$ ligand in **4d** can readily be replaced by PhNHOH (reaction (15) in Scheme 3), as revealed by the reaction of **4d** with four equivalents of PhNHOH, which afforded **5d** as the predominant porphyrin species within ten minutes.

Evidently, when the system contains an excess of PhNHOH, reaction (12) will lead to partial liberation of the bound PhNO in **3**, whereas reaction (15) will result in liberation of $PhNH_2$ in **4**. The facile reaction of free PhNO with PhNHOH to form PhN(O)=NPh, reaction (16),[54] probably accounts for both the formation of the azoxybenzene in the system and the absence of PhNO in the presence of a large excess of PhNHOH (as in the aforementioned catalytic disproportionation of the hydroxylamine in the presence of 2 mol% **3f**). Another feature of the "**1** + PhNHOH" system lies in the unobserved condensation of PhNO and $PhNH_2$ to form azobenzene (PhN=NPh). Such a condensation was found to occur rapidly and accompany the rapid formation of PhN(O)=NPh by reaction (16) in the photochemical disproportionation of PhNHOH.[55]

The observation of complexes **5** not only discloses the feasible ligation of *N*-arylhydroxylamine by a metalloporphyrin, but also provides an unprecedented coordination of *N*-substituted hydroxylamine to ruthenium. Previously, a handful of metal hydroxylamine complexes were observed or isolated,[19, 22, 23, 56–58] of which only one, [$Ru^{II}(CO)_2(PPh_3)_2(NH_2OH)Cl]^+$,[57] contains a ruthenium center; however, this is an *organometallic* compound coordinating the *unsubstituted* NH_2OH. Although complexes **5** were clearly observed only in the presence of free PhNHOH and were not isolated in pure forms, their Ru–NH(OH)Ph moieties are surprisingly robust, even more robust than the Fe–NH(OH)*i*Pr moiety in the iron porphyrin **7**, which bears a more strongly basic *N*-alkylhydroxylamine.[19] For example, no rapid exchange between the coordinated PhNHOH in **5** and the free PhNHOH in solution was observed at room temperature (see Figure 6a), in contrast to the case of complex **7** whose *i*PrNHOH axial ligand rapidly exchanges with free *i*PrNHOH even at −63 °C.[19] Since *N*-substituted hydroxylamines are known to coordinate with cytochrome P-455,[59] the formation of complexes **7** and **5** (the only observed *N*-alkyl- and *N*-arylhydroxylamine complexes of synthetic metalloporphyrins, respectively) should be of significance.

Reaction of dioxoruthenium(VI) porphyrins with NH_2OH: Unlike the reactions of complexes **1** with PhNHOH that form nitrosobenzene complexes, treatment of the dioxo complexes (**1a** or **1f**) with NH_2OH (generated in situ from $NH_2OH \cdot HCl + Et_3N$) afforded nitrosylruthenium(II) porphyrins **6a** or **6f** in moderate yields (reaction (17) in Scheme 4). The binding of nitrosyl group to ruthenium porphyrins has been a subject of extensive investigations in recent years,[60, 61] which led to isolation of a good number of nitrosylruthenium(II) porphyrins including **6a** (all from a direct reaction with nitric oxide).

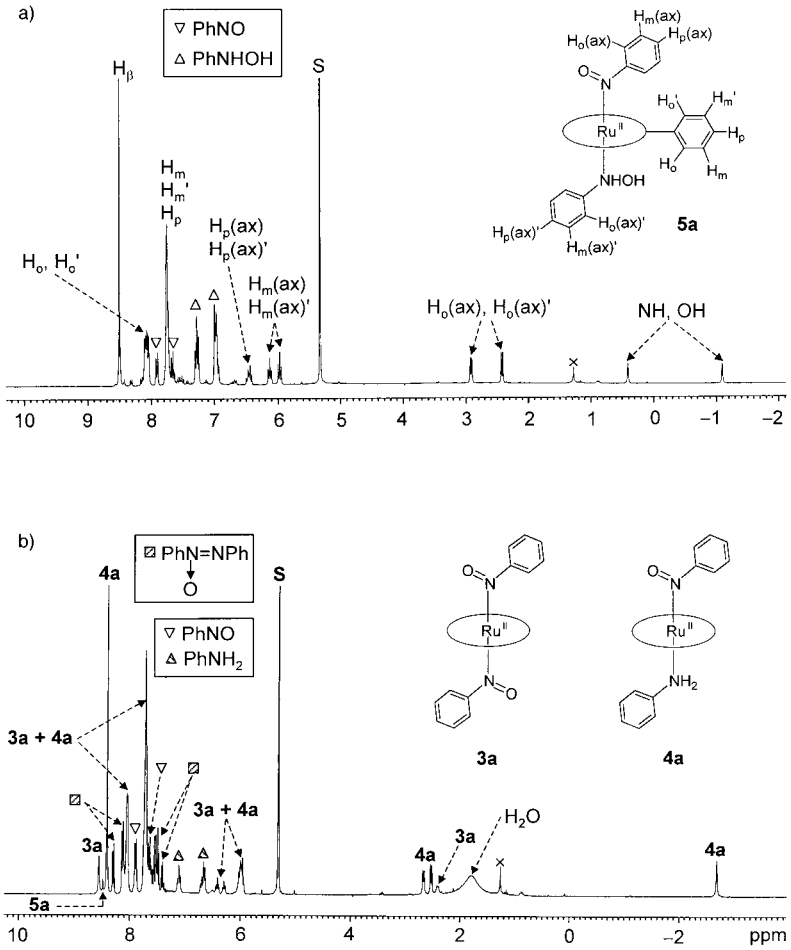
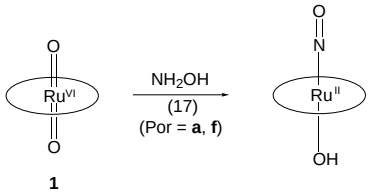


Figure 6. ^{1}H NMR spectra of a mixture of complex **3a** and PhNHOH (4 equiv) in CD_2Cl_2 after a) 10 min and b) 2 h. The peaks at $\delta = 0.40$ and -1.09 in a) and the broad peak at $\delta \sim 1.8$ in b) all disappeared when D_2O was added to the mixture. Note that no TMS was added to the deuterated solvent.



Scheme 4. Reaction of complexes **1** with NH_2OH to form nitrosylruthenium(II) porphyrins.

However, reaction (17) uniquely generates a nitrosylruthenium(II) porphyrin from oxidation of NH_2OH, a reactivity similar to the formation of the nitrosyl complex of myoglobin from NH_2OH in the presence of hydrogen peroxide.[62] It should be noted that while some *nonporphyrin* oxometal complexes were reported to react with NH_2OH to form metal nitrosyl complexes,[63, 64] complexes **1** are the only isolated oxometalloporphyrins that exhibit a similar reactivity.

Complex **6f** gives an intense ν(NO) band at ~ 1830 cm^{-1} in its IR spectrum, like the previously reported complex **6a**.[61] The "oxidation-state marker" band of **6f** is located at 1020 cm^{-1}, a frequency markedly higher than that of the nitrosoarene analogue **3f** (1013 cm^{-1}). This is in accord with the stronger π-acid character of the nitrosyl ligand. In the mass spectrum of **6f**, the peaks assignable to the parent ion $[M]^+$ and the fragments $[M - OH]^+$ and $[M - OH - NO]^+$ are all observed.

Conclusion

Interactions between dioxoruthenium(VI) porphyrins [$Ru^{VI}O_2$(Por)] (**1**) and excess *N*-phenylhydroxylamine result in formation of nitrosobenzene complexes [Ru^{II}(Por)(PhNO)$_2$] (**3**), [Ru^{II}(Por)(PhNO)(PhNH$_2$)] (**4**), and [Ru^{II}(Por)(PhNO)(PhNHOH)] (**5**) accompanied by catalytic disproportionation of the *N*-arylhydroxylamine into azoxybenzene and aniline. Complexes **3** and **4** have been isolated in pure forms; their structures both feature unidentate nitrosoarene coordination, in contrast to the η^2-nitrosoarene coordination of all the structurally characterized ruthenium nitrosoarene complexes reported in the literature. The long Ru–N(PhNO) bond and unusually short N–O bond in **4** (Por = 4-MeO-TPP) is striking in view of the possible presence of a push-pull effect beneficial to the Ru → N(O)Ph back-bonding in the complex due to the strong π-acid character of PhNO and the Lewis base character of aniline. The direct observation of **5** (by ^{1}H NMR spectroscopy), whose ligated PhNHOH group undergoes no rapid exchange with free PhNHOH in the solution at room temperature, creates a precedent for coordination of *N*-substituted hydroxylamines to ruthenium. In contrast to the reaction of **1** with *N*-phenylhydroxylamine, the reaction between **1** and the unsubstituted hydroxylamine gives rise to [Ru^{II}(Por)(NO)(OH)] (**6**), providing a novel access to nitrosylruthenium(II) porphyrins.

Experimental Section

General: All the reactions were performed at room temperature. Hydroxylamine hydrochloride (99%, Aldrich), triethylamine (99%, Acros), aniline (99%, Aldrich), nitrosobenzene (97%, Aldrich), and all the solvents (AR grade) were used as received. *N*-Phenylhydroxylamine[65] and complexes **1a**–**f**[1, 2, 4, 6] were prepared according to the literature methods. ^{1}H NMR spectra were recorded on a Bruker DPX 300 spectrometer (300 MHz) with $CDCl_3$ or CD_2Cl_2 as the solvent (containing tetramethylsilane (TMS) unless otherwise stated). The chemical shifts (δ) are reported relative to TMS. IR spectra were measured on a Bio-Rad FT-IR spectrometer (KBr pellet). UV/Vis spectra were recorded on a

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Hewlett–Packard 8452A diode-array spectrometer. Mass spectra were measured on a Finnigan LCQ quadruple ion-trap (electrospray) or Finnigan MAT 95 (FAB, matrix: 3-nitrobenzyl alcohol) mass spectrometer. Elemental analyses were performed by the Institute of Chemistry, the Chinese Academy of Sciences.

Isolation of bis(nitrosobenzene)ruthenium(II) porphyrins 3: A mixture of complex **1** (0.05 mmol) and *N*-phenylhydroxylamine (33 mg, 0.3 mmol) in chloroform (15 mL) was stirred for 2 h. After removal of the solvent, the residue was purified by chromatography on a column of silica gel with dichloromethane/hexane (2:1 v/v) as the eluent, affording the desired products in 40–93% yields.

(*meso*-Tetraphenylporphyrinato)bis(nitrosobenzene)ruthenium(II) (3a): Yield: 83%; UV/Vis (6.65×10^{-6} M, CH_2Cl_2): λ_{max} (log ε) = 410 (5.26), 514 (4.03), 602 nm (3.74, sh); IR: $\tilde{\nu}$ = 1010 cm^{-1} ("oxidation-state marker" band); ESMS: *m*/*z*: 821 $[M-\mathrm{PhNO}]^+$, 714 $[M-2\,\mathrm{PhNO}]^+$; elemental analysis calcd (%) for $C_{56}H_{38}N_6O_2Ru$ (928.01): C 72.48, H 4.13, N 9.06; found C 72.53, H 4.13, N 9.08.

(*meso*-Tetrakis(*p*-tolyl)porphyrinato)bis(nitrosobenzene)ruthenium(II) (3b): Yield: 82%; UV/Vis (9.10×10^{-6} M, CH_2Cl_2): λ_{max} (log ε) = 413 (5.21), 516 (4.04), 592 nm (3.76, sh); IR: $\tilde{\nu}$ = 1011 cm^{-1} ("oxidation-state marker" band); ESMS: *m*/*z*: 983 $[M-\mathrm{H}]^+$, 878 $[M-\mathrm{PhNO+H}]^+$, 770 $[M-2\,\mathrm{PhNO}]^+$; elemental analysis calcd (%) for $C_{60}H_{46}N_6O_2Ru$ (984.12): C 73.23, H 4.71, N 8.54; found C 72.93, H 4.89, N 9.01.

(*meso*-Tetrakis(*p*-chlorophenyl)porphyrinato)bis(nitrosobenzene)ruthenium(II) (3c): Yield: 84%; UV/Vis (7.51×10^{-6} M, CH_2Cl_2): λ_{max} (log ε) = 412 (5.22), 515 (4.05), 597 nm (3.72, sh); IR: $\tilde{\nu}$ = 1010 cm^{-1} ("oxidation-state marker" band); ESMS: *m*/*z*: 990 $[M-\mathrm{Ph+H}]^+$, 959 $[M-\mathrm{PhNO}]^+$, 852 $[M-2\,\mathrm{PhNO}]^+$; elemental analysis calcd (%) for $C_{56}H_{34}Cl_4N_6O_2Ru$ (1065.79): C 63.11, H 3.22, N 7.88; found C 63.54, H 3.47, N 8.16.

(*meso*-Tetrakis(2,6-dichlorophenyl)porphyrinato)bis(nitrosobenzene)ruthenium(II) (3e): Yield: 40%; UV/Vis (4.32×10^{-6} M, CH_2Cl_2): λ_{max} (log ε) = 410 (5.30), 530 (4.05), 580 nm (3.75, sh); IR: $\tilde{\nu}$ = 1008 cm^{-1} ("oxidation-state marker" band); ESMS: *m*/*z*: 1097 $[M-\mathrm{PhNO}]^+$, 989 $[M-2\,\mathrm{PhNO}]^+$.

(*meso*-Tetrakis(pentafluorophenyl)porphyrinato)bis(nitrosobenzene)ruthenium(II) (3f): Yield: 93%; UV/Vis (1.40×10^{-5} M, CH_2Cl_2): λ_{max} (log ε) = 407 (5.15), 533 (4.24), 573 nm (4.07, sh); IR: $\tilde{\nu}$ = 1013 cm^{-1} ("oxidation-state marker" band); ESMS: *m*/*z*: 1288 $[M]^+$, 1181 $[M-\mathrm{PhNO}]^+$, 1074 $[M-2\,\mathrm{PhNO}]^+$; elemental analysis calcd (%) for $C_{56}H_{18}F_{20}N_6O_2Ru\cdot0.5\,C_6H_{14}$ (1330.91): C 53.24, H 1.89, N 6.34; found C 53.00, H 1.59, N 6.72.

Isolation of mono(nitrosobenzene)ruthenium(II) porphyrin 4d: This procedure was identical to that for the isolation of complexes **3**, except that dichloromethane/methanol (96:4 v/v) was used as the eluent (in this case no ruthenium porphyrin could be eluted by dichloromethane/hexane mixture).

(*meso*-Tetrakis(*p*-methoxyphenyl)porphyrinato)(nitrosobenzene)(aniline)-ruthenium(II) (4d): Yield: 78%; UV/Vis (3.43×10^{-6} M, CH_2Cl_2): λ_{max} (log ε) = 414 (5.36), 535 (3.99), 612 nm (3.61, sh); IR: $\tilde{\nu}$ = 3340 (NH), 3284 (NH), 1006 cm^{-1} ("oxidation-state marker" band); ESMS: *m*/*z*: 1034 $[M]^+$, 941 $[M-\mathrm{PhNH_2}]^+$, 834 $[M-\mathrm{PhNO}-\mathrm{PhNH_2}]^+$; elemental analysis calcd (%) for $C_{60}H_{48}N_6O_5Ru\cdot4/3\,CH_2Cl_2$ (1147.37): C 64.20, H 4.45, N 7.32; found C 64.69, H 4.40, N 7.41.

Isolation of mono(nitrosobenzene)ruthenium(II) porphyrin 4b: A solution of complex **1b** (0.06 mmol) and PhNHOH (0.6 mmol) in chloroform (10 mL) was stirred at room temperature for 24 h. The resulting dark red solution was concentrated to ~2 mL followed by addition of ethanol (10 mL). After the mixture was kept open to the atmosphere overnight, the purple solid precipitated was collected by filtration, washed with ethanol and dried.

(*meso*-Tetrakis(*p*-tolyl)porphyrinato)(nitrosobenzene)(aniline)ruthenium(II) (4b): Yield: 64%; UV/Vis (5.8×10^{-6} M, CH_2Cl_2): λ_{max} (log ε) = 413 (5.29), 533 (4.32), 602 nm (3.68, sh); IR: $\tilde{\nu}$ = 3345 (NH), 3278 (NH), 1008 cm^{-1} ("oxidation-state marker" band); ESMS: *m*/*z*: 970 $[M]^+$, 877 $[M-\mathrm{PhNH_2}]^+$, 770 $[M-\mathrm{PhNO}-\mathrm{PhNH_2}]^+$.

Isolation of nitrosylruthenium(II) porphyrins 6: Complex **1a** or **1f** (0.05 mmol) was added to a solution of $NH_2OH\cdot HCl$ (21 mg, 0.3 mmol) in chloroform (15 mL) containing triethylamine (0.43 mL, 3 mmol). The mixture was stirred for 2 h at room temperature and then evaporated to dryness. Column chromatography of the residual solid on silica gel by using dichloromethane/methanol (98:2 v/v) as the eluent afforded the desired product in moderate yield.

(*meso*-Tetraphenylporphyrinato)(hydroxy)(nitrosyl)ruthenium(II) (6a): Yield: 65%; the spectral data of this complex are identical to those reported in ref. [61].

(*meso*-Tetrakis(pentafluorophenyl)porphyrinato)(hydroxy)(nitrosyl)ruthenium(II) (6f): Yield: 35%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.01 (s, 8H; H_β); UV/Vis (1.02×10^{-5} M, CH_2Cl_2): λ_{max} (log ε) = 405 (5.21), 551 nm (4.26); IR: $\tilde{\nu}$ = 1832 (NO), 1020 cm^{-1} ("oxidation-state marker" band); FAB MS: *m*/*z*: 1121 $[M]^+$, 1104 $[M-\mathrm{OH}]^+$, 1074 $[M-\mathrm{OH}-\mathrm{NO}]^+$.

In situ reaction of complexes 1 with PhNHOH: A mixture of **1d** (4.3 mg, 5×10^{-3} mmol) and PhNHOH was dissolved in $CDCl_3$ (0.5 mL). The resultant solution was stirred for 2 h and then examined by ^{1}H NMR spectroscopy. The products formed in the system depended on the equivalents of starting PhNHOH: 1) two equivalents: **3d** and **4d** in ~4:1 molar ratio, and 2) six equivalents: **4d** and **3d** in ~2:1 molar ratio, accompanied by the formation of free PhNO, $PhNH_2$, and PhN(O)=NPh. In both cases, the starting PhNHOH was completely consumed. The reaction of **1b** with six equivalents of PhNHOH was also examined, which is similar to the case of **1d** under similar conditions.

In situ reaction of complexes 3 with PhNHOH: PhNHOH (4 equiv) was added to a solution of **3a** (5×10^{-3} mmol) in $CDCl_3$ (0.5 mL). The mixture was shaken for 5 min and examined by ^{1}H NMR spectroscopy, which revealed that **3a** was almost quantitatively converted into **5a** within 10 min, with concomitant formation of free PhNO. After the mixture was kept for 2 h, **5a** was almost completely changed into a mixture of **3a** and **4a** in ~1:8 molar ratio accompanied by formation of free $PhNH_2$ and PhN(O)=NPh (PhNHOH was not detected). Similar phenomenon was also observed for **3b** and **3f**. In a typical catalytic experiment, complex **3f** was treated with 50 equivalents of PhNHOH under argon for 3 days, resulting in a ~50% conversion of the hydroxylamine to PhN(O)=NPh and $PhNH_2$ and a complete conversion of **3f** into a mixture of **4f** and **5f** with **4f**:**5f**:(PhN(O)=NPh):$PhNH_2$ molar ratio of ~1:2:28:22.

In situ reaction of complexes 3 with $PhNH_2$: $PhNH_2$ (6 equiv) was added to a solution of **3b** or **3f** (5×10^{-3} mmol) in $CDCl_3$ (0.5 mL). The mixture was shaken for 5 min and examined by ^{1}H NMR spectroscopy, which revealed the formation of **4b** or **4f** as the only detectable porphyrin species, with concomitant formation of free PhNO.

In situ reaction of complex 4d with PhNO or PhNHOH: PhNO or PhNHOH (4 equiv) was added to a solution of **4d** (5.2 mg, 5×10^{-3} mmol) in $CDCl_3$ (0.5 mL). The mixture was shaken for 5 min and examined by ^{1}H NMR spectroscopy. For the reaction with PhNO, a mixture of **3d** and **4d** in ~1:1 molar ratio was observed, whereas for that with PhNHOH, **5d** was found to be the predominant porphyrin species (only traces of **4d** was detected).

X-ray crystal structure determinations of 3a, 3e, and 4d: Single crystals of complex **3a** were obtained by slow evaporation of a solution of the complex in dichloromethane, whereas those of **3e** and **4d** were obtained in the forms **3e**$\cdot CH_2Cl_2\cdot CHCl_3$ and **4d**$\cdot 2\,CHCl_3$ by slow diffusion of hexane into solutions of **3e** and **4d** in chloroform/dichloromethane mixtures. In the case of **3a**, the data were collected at 301 K on a Rigaku AFC7R diffractometer by using a crystal of dimensions $0.30\times0.15\times0.10$ mm. The structure was refined by full-matrix least-squares on *F* with the software package TeXsan[66] on a Silicon Graphics Indy computer. For the latter two complexes, data collection was made at 294 K on a Bruker SMART CCD diffractometer by employing a crystal of the dimensions $0.20\times0.16\times0.14$ (**3e**$\cdot CH_2Cl_2\cdot CHCl_3$) and $0.20\times0.16\times0.14$ mm (**4d**$\cdot 2\,CHCl_3$). The structures were refined by full-matrix least-squares on F^2 with the SHELXL-97 program. In all the three cases a graphite monochromatized $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) was used.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-150796 (**3a**), CCDC-150797 (**3e**), and CCDC-150798 (**4d**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was supported by The University of Hong Kong and the Hong Kong Research Grants Council (HKU 7096/97P and HKU 7099/00P).

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[31] The starting PhNHOH used for the reactions contained no $PhNH_2$, as indicated by ^{1}H NMR spectroscopy, and TLC and GC measurements. The $PhNH_2$ ligand in **4a** must be one of the products in the "**1d** + PhNHOH" reaction system.
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Received: October 12, 2000 [F2795]