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Dioxygen and Nitric Oxide Complexes of Rhodium Porphyrins

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$(RhOEP)_2$ (OEP = octaethylporphyrin) reacts with dioxygen to form $RhOEP(O_2)$ ($S = {}^1/_2$), which subsequently forms the μ-peroxo complex $(RhOEP)_2O_2$. EPR studies of $RhOEP(O_2)$ and $RhTPP(O_2)$ (TPP = tetraphenylporphyrin) and their 1:1 donor complexes are reported and compared with those of the cobalt analogues. $(RhOEP)_2$, RhOEP(H), and RhOEP(Cl) all react with nitric oxide to ultimately produce the same product, RhOEP(NO). The reactions of RhOEP(Cl) and RhTPP(Cl) with nitric oxide proceed through a metastable paramagnetic intermediate Rh(por)(Cl)(NO) (por = porphyrin), which from EPR and electronic spectral studies is formulated as containing a porphyrin π-cation radical unit with an ${}^2A_{1u}$ ground state. RhOEP(NO)(Cl) associates to form a radical dimer ($S = 1$) with $D = 5.17 \times 10^{-3}$ cm^{-1} and $E = 2.4 \times 10^{-4}$ cm^{-1}, but only monomeric RhTPP(NO)(Cl) is observed. Electrochemical studies of rhodium(III) porphyrins also support the porphyrin cation radical formulation for Rh(por)(NO)(Cl) complexes.

Introduction

Binding and activation of diatomic molecules by metalloporphyrins have attracted wide interest due to the potential importance of these species in thermal and photocatalytic reactions including biologically important processes.[1-4] Our interest in these systems has been focused on systematically observing the scope of diatomic molecule complexes accessible to metalloporphyrins and revealing unifying features of their physical and chemical properties.[2-6]

The emerging central role of rhodium complexes in catalysis has prompted our general study of rhodium macrocycle species and their reactivity with small molecules.[6] One focal point of this program is in exploring the radical-like reactivity patterns of planar low-spin d^7 complexes of rhodium(II) and in making comparisons with the better characterized cobalt(II) chemistry.[5-7] While cobalt(II) porphyrins are invariably monomeric ($S = {}^1/_2$) species, the only reported Rh^{II} porphyrin is a Rh–Rh bonded dimer, $(RhOEP)_2$.[8] Formation of the metal–metal bonded dimer is one manifestation of the enhanced covalent-bond-forming properties of the second-transition-series metal. Although no monomeric Rh^{II} porphyrins are yet available, $(RhOEP)_2$, RhOEP(H), and RhOEP(Cl) and RhTPP(Cl) all react as potential sources of the Rh^{II} porphyrin unit. This paper reports on the reactions of rhodium octaethylporphyrin (RhOEP) and rhodium tetraphenylphorphyrin (RhTPP) species with nitric oxide and dioxygen.

Experimental Section

Rhodium tetraphenylporphyrin chloride (RhTPP(Cl)) and rhodium octaethylporphyrin chloride ((RhOEP(Cl)) were prepared by the method of Sadasivan and Fleisher.[9] Purification was achieved by chromatography of the crude product on alumina.

$RhTPP(O_2)$ was prepared by following the method of James and Stynes.[10] The crude product was purified on an alumina chromatography column.

RhOEP(H) was prepared from RhOEP(Cl) by following the methods of Ogoshi et al.[8] The orange precipitate was washed twice with deoxygenated ethanol and dried under vacuum prior to use.

$(RhOEP)_2$ was prepared by using a 75-W sunlamp to photolyze RhOEP(H) in degassed toluene thermostated to 25 ± 1 °C. Formation of $(RhOEP)_2$ is followed by observing the appearance of the characteristic AB multiplet at 4.64 and 4.20 ppm below Me_4Si due to the diastereotopic $-CH_2-$ protons on the porphyrin's periphery. Both the low-field RhOEP(H) methine peak at 10.33 ppm and the upfield $-CH_3$ triplet resonance at 2.13 ppm shift to higher fields (9.46 and 1.93 ppm, respectively) upon dimer formation due to increased shielding of the protons.

Nitric oxide complexes were formed by exposing toluene solutions or pure solid metalloporphyrin complexes to 200–700 mm of nitric oxide.

CP grade nitric oxide was purchased from Matheson Gas Products and was passed through a column of KOH pellets to free it of higher nitrogen oxides. Toluene was dried over P_2O_5 and vacuum distilled. Dichloromethane (Fisher) was distilled over P_2O_5 prior to use. Tetra-*n*-butylammonium perchlorate (TBAP) was prepared by the reaction of tetra-*n*-butylammonium chloride and perchloric acid in distilled water. The precipitate was recrystallized three times from hot ethanol solutions and stored under vacuum. Perdeuterated toluene (99%) was obtained from Merck and Co. and was degassed prior to use. Other reagents were used as supplied.

Differential-pulse polarograms were obtained on a Princeton Applied Research Polarographic analyzer, Model 174A, with a standard three-electrode cell. Electrochemical measurements were made with use of a glassy carbon working electrode vs. the saturated calomel electrode (SCE). The polarograms were scanned at a rate of 20 mV/s. Exhaustive electrolysis was performed on a Princeton Applied Research digital coulometer, Model 179, using a platinum mesh electrode vs. SCE. All electrochemical experiments were performed under an argon atmosphere at 25 ± 1 °C.

Fourier transform NMR experiments were performed on a Japan Electron Optics Laboratory JNM-PS-100 spectrometer with an associated EC-100 computer. Magnetic susceptibilities were measured by the Evans NMR method.[11]

Instrumentation and procedures for obtaining EPR, electronic, and infrared spectra have been described previously.[5,6]

Results and Discussion

$(RhOEP)_2$ Reactions with Dioxygen. When dry oxygen is allowed to slowly diffuse into a cold toluene solution (−80 °C) of $(RhOEP)_2$, electronic spectral changes occur (Figure 1), accompanied by the appearance of an EPR spectrum ($\langle g \rangle = 2.032$). Freezing this toluene solution (−160 °C) results in an EPR spectrum with three g values ($g_1 = 2.100$, $g_2 = 2.010$, $g_3 = 1.988$) characteristic of an end-on coordinated dioxygen species similar to HO_2 and $CoTPP(O_2)$ (Figure 2).[4,5] The dioxygen complex is formulated as $RhOEP(O_2)$ and described

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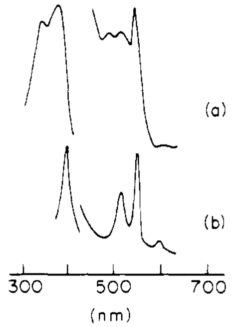

Figure 1. Electronic spectra in toluene solution for (a) $(RhOEP)_2$ (25 °C) and (b) $RhOEP(O_2)$ (−20 °C).

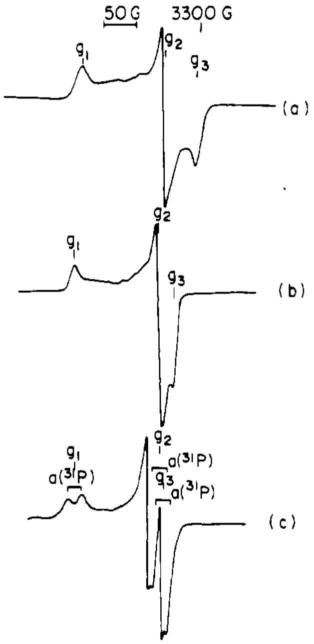

Figure 2. EPR spectra in frozen toluene media (100 K) for (a) $RhOEP(O_2)$, (b) $RhOEP(O_2)(pip)$, and (c) $RhOEP(O_2)(P(OBu)_3)$.

as a Rh(III) complex, $(OEP)Rh^{III}O_2^-$. When toluene is pumped off at low temperatures (−20 °C) from a solution of $RhOEP(O_2)$, the resulting solid is predominantly $RhOEP(O_2)$. The IR spectrum of this solid shows a new band centered at 1075 cm^{-1}, which, although partially obscured by ligand bands, is tentatively assigned to the ν_{O-O} stretching frequency in $RhOEP(O_2)$. The ν_{O-O} stretching frequency in an analogous cobalt(II) dioxygen complex appears at 1137 cm^{-1}.[12]

When solutions of $RhOEP(O_2)$ are warmed to 20 °C, the EPR signal diminishes in intensity and eventually disappears. The presence of donor molecules accelerates this process. the resulting diamagnetic complex has electronic and ^1H NMR spectra characteristic of a $Rh^{III}OEP$ species and is formulated as the μ-peroxo complex $(RhOEP)_2O_2$. Bridging peroxo complexes of cobalt(III) and rhodium(III) have been characterized previously.[13,14] The ν_{O-O} band was not observed in the IR spectrum of this μ-peroxo complex, which is consistent with complexes of this type.[15]

Donor molecule complexes of $RhOEP(O_2)$ are produced by first forming $RhOEP(O_2)$ at −80 °C with subsequent addition of base. EPR spectra and parameters for selected nitrogen and phosphorus donors appear in Figure 2 and Table I. Phosphorus-31 nuclear hyperfine coupling in the alkylphosphine and alkyl phosphite donor complexes of $RhOEP(O_2)$ establishes clear parallels with the cobalt(II) dioxygen complexes.

Table I. EPR *g* Values for $RhOEP(O_2)$ and $RhTPP(O_2)$ Complexes

complex	g_1[a]	g_2[a]	g_3[a]	g_{iso}
$RhOEP(O_2)$	2.100	2.010	1.988	2.030
$RhTPP(O_2)$	2.084	2.025	1.993	2.033
$RhOEP(O_2)(pip)$[b]	2.094	2.010	1.996	2.031
$CoTPP(O_2)(py)$[c]	2.072	2.003	2.003	
$RhOEP((BuO)_3P)(O_2)$	2.084 (21. (21.6)[d]	2.004 (21.6)	2.000 (23.7)	2.032 (23.7)
$CoTPP((BuO)_3P)(O_2)$[e]				2.016 (31.4)
$RhTPP(O_2)((EtO)_3P)$	2.086 (~0)	2.009 (35.5)	2.004 (35.5)	2.032 (23.7)
$CoTPP(O_2)(EtO)_3P)$[e]				2.020 (29.1)
$Co(acacen)(O_2)(H_2O)$[f]	2.087	1.996	1.996	2.027
$[(Co(en)_2)_2O_2]^{5+}$[g]	2.079	2.023	2.010	2.037
$[(Rh(bpy)_2Cl)_2O_2]^{3+}$[h]	2.088	2.020	1.992	2.032

[a] *g* values are ±0.001. [b] pip = piperidine. [c] B. M. Hoffman and D. H. Petering, *Proc. Natl. Acad. Sci. U.S.A.* 95, 1796 (1973). py = pyridine. [d] Values in parentheses refer to $A(^{31}P)$ in gauss. [e] From B. B. Wayland and M. E. Ald-Elmageed, *J. Am. Chem. Soc.*, 96, 4809 (1974). [f] B. M. Hoffman, D. L. Diemente, and F. Basolo, *ibid.*, 92, 61 (1970). [g] D. H. Huchital and A. E. Martell, *Inorg. Chem.*, 13, 2965 (1974). en = ethylenediamine. [h] H. Caldonaru, K. DeArmond, and K. Henck, *ibid.*, 17, 2030 (1978). bpy = bipyridine.

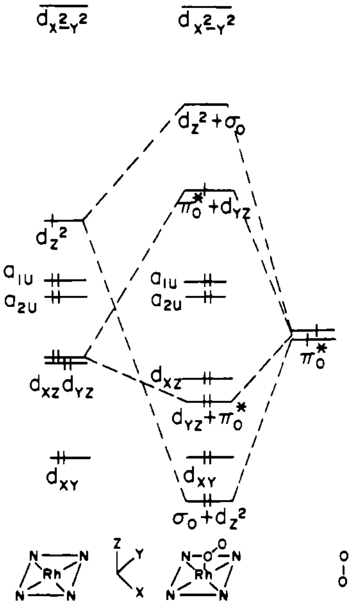

Figure 3. Schematic MO diagram for $Rh(por)(O_2)$ complexes.

$RhTPP(O_2)$ complexes can be prepared by borohydride reduction of any $Rh^{III}TPP(X)$ complex with subsequent addition of dioxygen. EPR parameters for $RhTPP(O_2)$ and selected donor adducts appear in Table I.

A schematic MO diagram for $Rh(por)O_2$ appears in Figure 3. The highest energy electron occupies the dioxygen π^* orbital, and the O_2 ligand is thus formulated as a coordinated superoxide ($Rh^{III}O_2^-$). Dioxygen complexes of "Rh^{II}" porphyrins are closely related to those of the isoelectronic Co^{II} porphyrins, except that the enhanced covalent-bond-forming property of the second-transition-series metal results in greater thermal stability for the rhodium dioxygen complexes.

Reaction of Nitric Oxide with $(RhOEP)_2$. The addition of

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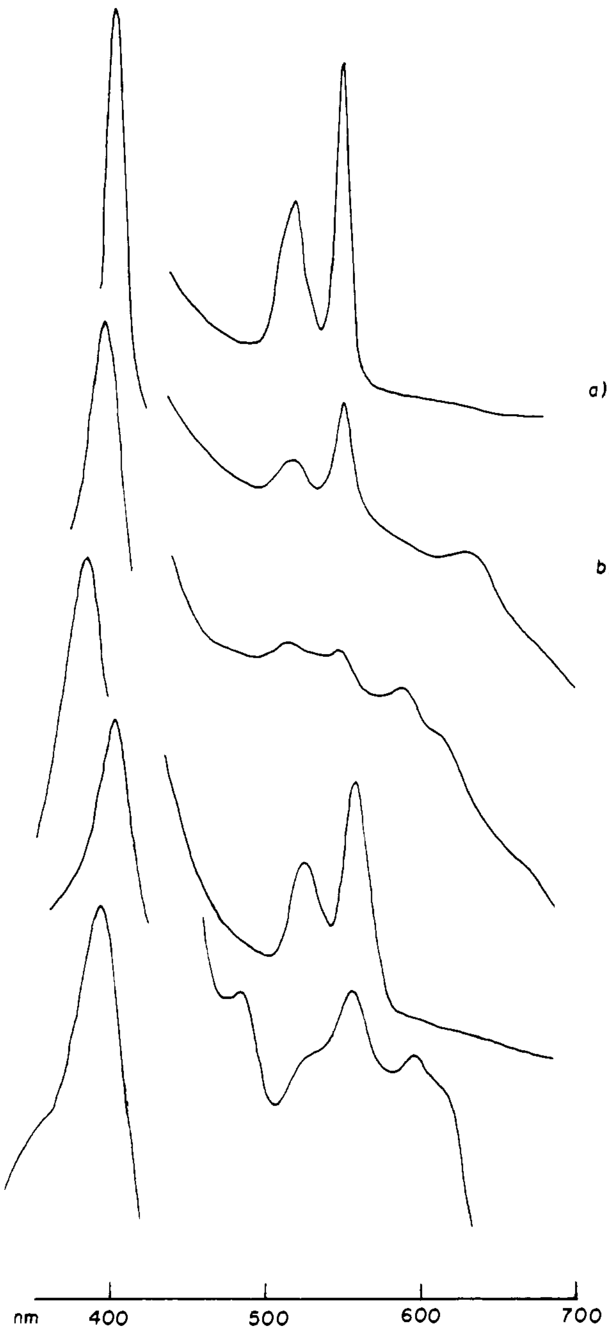


Figure 4. Electronic spectra for (a) RhOEPCl, (b) RhOEP(Cl) + NO (300 torr), (c) $[RhOEP(NO)]^+$ generated by electrolysis of RhOEP(NO) in CH_2Cl_2 with TBAP electrolyte, (d) RhOEP(NO), and (e) RhOEP(NO) + NO (300 torr). All spectra except (c) are determined in toluene solution at 298 K.

nitric oxide to degassed toluene solutions of $(RhOEP)_2$ immediately produces a new electronic absorption spectrum (Figure 5d) characteristic of a rhodium(III) porphyrin species. An infrared spectrum of the isolated reaction product reveals a new peak at 1630 cm^{-1} assigned to the nitric oxide stretch. A degassed Nujol mull of $(RhOEP)_2$ also reacts with nitric oxide to form a complex with an infrared band at 1630 cm^{-1}. Measurement of the magnetic susceptibility indicates that the nitric oxide complex is diamagnetic. The new complex is identified as RhOEP(NO) ($S = 0$), which is isoelectronic with CoTPP(NO) ($\nu_{NO} = 1690$ cm^{-1})[7,8] and electronically related to $RhCl_2(PPh_3)_2(NO)$ ($\nu_{NO} = 1620$ cm^{-1}).[9]

Solutions of RhOEP(NO) were found to be air sensitive. Exposure of RhOEP(NO) to oxygen results in the slow loss of the nitric oxide stretch (1630 cm^{-1}) and the concomitant

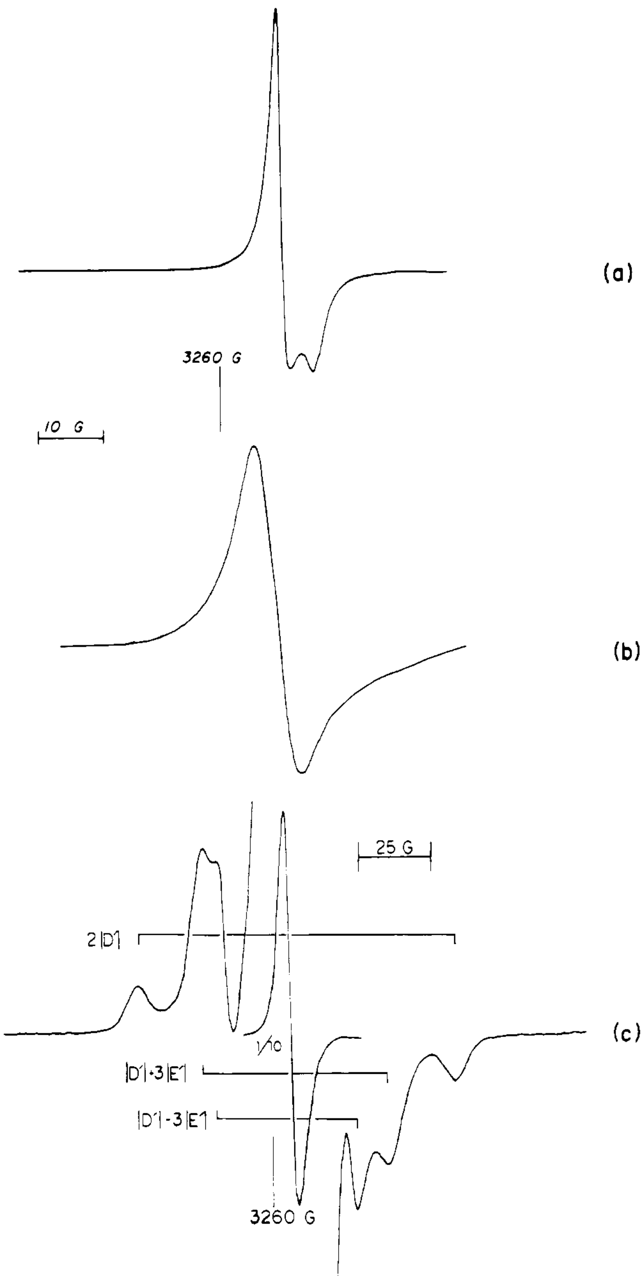
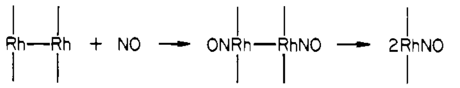


Figure 5. EPR spectra in frozen toluene media (100 K): (a) 10^{-8} M RhOEP(NO) + NO (300 torr); (b) 10^{-4} M RhOEP(Cl) + NO (300 torr); (c) 2×10^{-3} M RhOEP(Cl) + NO (300 torr).

appearance of new infrared bands at 1222 and 1325 cm^{-1} characteristic of nitrite coordinated to the metal through the nitrogen.[15] Formation of nitro complexes represents electrophilic attack by O_2 on coordinated NO, which has been observed in related cobalt–NO complexes.[16]

Although no monomeric Rh^{II} porphyrin complexes have yet been observed, $(Rh^{II}OEP)_2$ reacts as a source of $Rh^{II}OEP$ in reactions of NO and O_2. The reaction of $(RhOEP)_2$ with NO probably proceeds by attack at an exterior coordination site and then rupture of the Rh–Rh bond (eq 1). The reaction

 (1)

$$\mathrm{Rh{-}Rh} + \mathrm{NO} \rightarrow \mathrm{ONRh{-}RhNO} \rightarrow \mathrm{2RhNO} \quad (1)$$

of dioxygen must occur in this manner because of the observed intermediacy of $RhOEP(O_2)$ in the ultimate formation of

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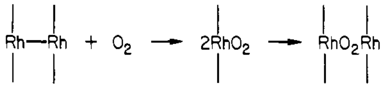
(16) S. Clarkson and F. Basolo, *Inorg. Chem.*, **12**, 1528 (1973).

$(RhOEP)_2O_2$ (eq 2). Initial attack on the Rh–Rh bond by



$$Rh{-}Rh + O_2 \rightarrow 2RhO_2 \rightarrow RhO_2Rh \qquad (2)$$

O_2 should have directly produced the peroxo complex, which is the thermodynamically favored product.

Reaction of Nitric Oxide with Rh(III) Porphyrins. RhOEP(H). RhOEP(H) in toluene solution or as a solid quickly reacts with nitric oxide (300 torr) to form RhOEP(NO) (eq 3). RhOEP(H) thus serves as an alternate to

$$2RhOEP(H) + 2NO \rightarrow 2RhOEP(NO) + H_2 \qquad (3)$$

$(RhOEP)_2$ as a source of $Rh^{II}OEP$ in reactions of nitric oxide. This reaction probably involves nitric oxide binding trans to the hydrogen and subsequent homolytic cleavage of the Rh–H bond, but no intermediates were spectroscopically observed in either the solution or solid-state reactions.

RhOEP(Cl), RhTPP(Cl). Addition of nitric oxide (300 torr) to degassed toluene solutions of RhOEP(Cl) results in the immediate appearance of an EPR signal (Figure 4) and a new broad electronic spectrum underlying the spectrum of residual RhOEP(Cl) (Figure 5). Quickly removing the solvent and nitric oxide results in the nearly quantitative recovery of RhOEP(Cl), indicative of reversible nitric oxide coordination (eq 4). If RhOEP(Cl) and NO remain in contact, the EPR signal slowly decreases in intensity and disappears in a period of several hours. Removal of the solvent results in isolation of RhOEP(NO) (eq 5). RhTPP(Cl) reacts with NO in a manner paralleling that of RhOEP(Cl) (eq 6, 7).

$$RhOEP(Cl) + NO \rightleftarrows RhOEP(Cl)(NO) \qquad (4)$$

$$RhOEP(Cl) + 2NO \rightarrow RhOEP(NO) + NOCl \qquad (5)$$

$$RhTPP(Cl) + NO \rightleftarrows RhTPP(Cl)(NO) \quad (S = {}^1/_2) \qquad (6)$$

$$RhTPP(Cl)(NO) + NO \rightarrow RhTPP(NO) + NOCl \qquad (7)$$

The radical-like EPR spectrum and broad electronic spectral bands associated with the intermediate NO complexes of RhOEP(Cl) and RhTPP(Cl) are similar to those previously observed for porphyrin π-cation radicals.[17–19] The intermediate is formulated as the mono(nitric oxide) complex RhOEP(Cl)(NO), where the incoming NO group intramolecularly oxidizes the porphyrin ligand to form a $(Rh^{III}OEP)^{2+}$ cation radical unit. Similar electronic and EPR spectra are observed for ruthenium and palladium alkylporphyrin π-cation radicals.[18a,d] The highest occupied π orbitals of the prophyrin are of a_{1u} and a_{2u} symmetry. Porphyrin π-cation radicals are known to adopt either the $^2A_{1u}$ or $^2A_{2u}$ state, depending on rather subtle effects of the porphyrin substituents and coordinated metal.[20] Absence of any nuclear hyperfine splitting in the EPR is characteristic of the $^2A_{1u}$ state.[19] An $^2A_{1u}$ ground state could result from stabilization of the a_{2u} MO of the porphyrin by mixing with the empty metal p_z (a_{2u}).

In order to clearly establish the nature of the porphyrin radical, we undertook an electrochemical investigation. The results of the experiments are presented in Table II. Electronic spectra for the exhaustive one-electron oxidation of rhodium(III) porphyrins are indicative of porphyrin π-cation radicals. No hyperfine is observed in any of the EPR spectra of generated π-cation radicals, which is consistent with an $^2A_{1u}$ ground state.

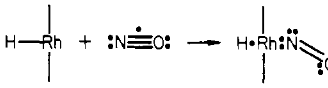
Table II. Oxidation Potentials for Rhodium(III) Porphyrin Complexes

complex	$\langle g\rangle^b$	$E_{1/2}$, V^a 1st oxidn	 2nd oxidn^c
H_2TPP		0.97	1.25
RhTPP(Cl)	2.001	0.98	1.36
RhTPP(NO)	2.001	0.94	1.36
H_2OEP		0.84	1.16
RhOEP(Cl)	2.001	0.82	1.34
RhOEP(NO)	2.001	0.77	1.27

[a] Values are ±0.01 V determined in CH_2Cl_2; glassy carbon working electrode vs. SCE, TBAP electrolyte. [b] *g* values (±0.001) are for porphyrin π-cation radicals generated by constant-potential electrolysis of the corresponding Rh(III) porphyrin in CH_2Cl_2 with TBAP present. Values of *n*, the number of electrons lost, average 0.95. [c] The second oxidation results in a diamagnetic complex, which is formulated as a porphyrin π dication.

When highly concentrated degassed toluene solutions of RhOEP(Cl) ($>10^{-3}$ M) are reacted with nitric oxide, an EPR signal of a triplet ($S = 1$) species with $D = 5.17 \times 10^{-3}$ cm^{-1} and $E = 2.4 \times 10^{-4}$ cm^{-1} appears superimposed over the $g = 2.001$ peak for the cation radical (Figure 5c). The triplet EPR spectrum is characteristic of a radical dimer and thus associated with the dimer of RhOEP(Cl)(NO). A radical dimer of RhTPP(Cl)(NO) was not observed, which probably reflects the increased steric requirements of tetraphenylporphyrin.

Reaction of nitric oxide with RhOEP(Cl) and RhTPP(Cl) ultimately produces RhOEP(NO). Observation of relatively stable paramagnetic intermediates formulated as $[(Rh^{III}(por))^{2+}(NO^-)(Cl^-)]$ differentiate the reactions of the $Rh^{III}Cl$ complexes from those of $(RhOEP)_2$ and RhOEP(H). The bonding orbitals for the Rh^{II}–Rh^{II} and the Rh–H bonds may be at relatively high energies such that the NO entering along the bond axis essentially pulls one electron from the Rh–H and Rh–Rh bonds in forming a coordinated NO^- unit (eq 8).


(8)

The strength of the Rh–Cl bond produces a high barrier for this reaction pathway, and the nitric oxide can alternatively form an NO^- by abstracting an electron from the porphyrin π system, producing $[(Rh^{III}(por))^{2+}(Cl^-)(NO^-)]$. In this reaction, the rhodium center achieves six-coordination and a favorable 18-valence-electron case. This intermediate then reacts slowly to produce the final product, Rh(por)(NO).

The d^6 metal centers in $Rh^{III}TPP(Cl)$ and $Fe^{II}TPP$ both add one nitric oxide to form $S = {}^1/_2$ species (Cl)RhTPP(NO) and FeTPP(NO). Although these complexes have the same number of valence electrons, their electronic configurations are very different. In developing a generalized MO scheme for diatomic molecule complexes of square-planar metallo species, we have previously considered only the metal d and diatomic π* orbitals, ignoring the macrocycle orbitals.[5,6] This has been adequate in describing the general features of a wide variety of diatomic molecule complexes. However, the porphyrin π orbitals are near in energy to the occupied metal d orbitals and central to describing Rh(por)(NO)(Cl) complexes. Schematic MO diagrams for FeTPP(NO) and RhTPP(NO)(Cl) appear in Figure 6. In the case of FeTPP(NO), the Fe–NO unit lies between the two limiting electron distributions, $Fe^{II}{\cdot}NO$ and Fe^INO^+, and the seven electrons from the metal d and NO π* orbitals remain on these two centers. In

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(17) J. H. Furhop, *Struct. Bonding*, (*Berlin*), **18**, 1 (1974).

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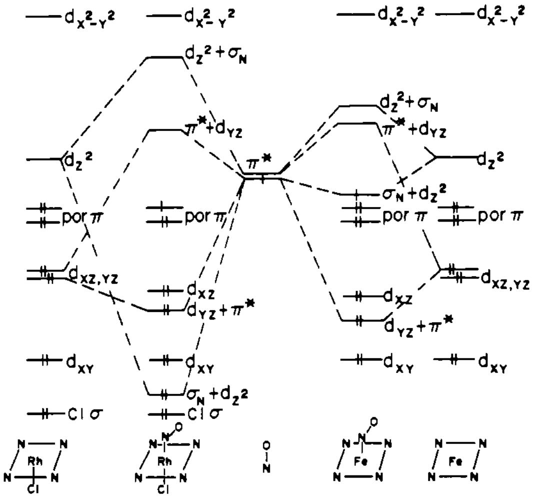

Figure 6. Schematic MO diagrams for Rh(por)(Cl)(NO) and Fe(por)-NO.

the case of RhTPP(Cl)(NO), a $Rh^{III}NO^-$ unit occurs by abstracting an electron from the porphyrin π system. This can be viewed as occurring because the Rh–NO covalent interaction is sufficiently strong to lower the $\sigma_N + d_{z^2}$ MO (Figure 6) below the porphyrin π orbitals. This results in transfer of a porphyrin π electron to the Rh–NO σ-bonding orbital and produces a $Rh^{III}NO^-$ unit.

RhOEP(NO), RhTPP(NO), and CoTPP(NO) in the Presence of Excess Nitric Oxide. RhOEP(NO) is formulated as $Rh^{III}OEP(NO^-)$, and the $Rh^{III}OEP$ unit in RhOEP(NO) is closely related electronically to that of RhOEP(Cl), $Rh^{III}OEP(Cl^-)$. RhOEP(NO) in toluene or chloroform near the solvent freezing point interacts reversibly with nitric oxide (eq 9) to form an $S = {}^1/_2$ species with the EPR and electronic

$$\text{RhOEPNO} + \text{NO} \rightleftarrows \text{RhOEP(NO)}_2 \quad (S = {}^1/_2) \qquad (9)$$

spectra given in Figures 4 and 5. This paramagnetic bis(nitric oxide) complex is formulated as $[(RhOEP)^{2+}(NO^-)_2]$ in analogy with $[(RhOEP)^{2+}(Cl^-)(NO^-)]$. Absence of nuclear hyperfine splitting is indicative of an $^2A_{1u}$ ground state for the porphyrin cation radical complex. RhTPP(NO) also undergoes reversible binding with NO to form an $S = {}^1/_2$ complex, $RhTPP(NO)_2$, with an EPR spectrum consistent with an $^2A_{1u}$ state. CoTPPNO can also bind a second NO to form $CoTPP(NO)_2$ (eq 10), which has the EPR spectrum shown

$$\text{CoTPPNO} + \text{NO} \rightleftarrows \text{CoTPP(NO)}_2 \qquad (10)$$

in Figure 7.[21] This species is formulated as $[(CoTPP)^{2+}(NO^-)_2]$ with the odd electron occupying an a_{2u} MO. Hyperfine splitting from cobalt in addition to porphyrin and nitric oxide nitrogens is consistent with an $^2A_{2u}$ ground state for $CoTPP(NO)_2$. The difference in ground states for $RhTPP(NO)_2$, $^2A_{1u}$, and $CoTPP(NO)_2$, $^2A_{2u}$, could result from rhodium being more effective than cobalt in using the p_z (a_{2u}) as an acceptor orbital for porphyrin a_{2u} π electrons.

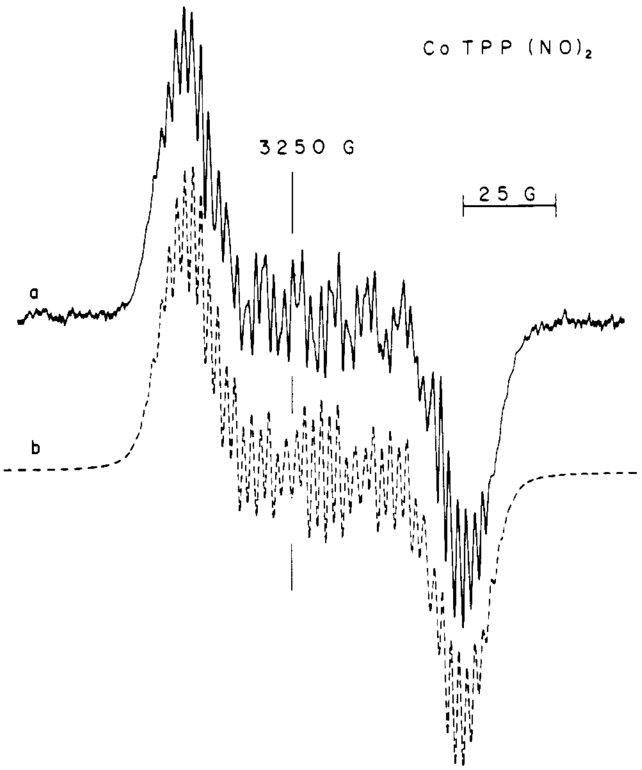

Figure 7. EPR spectrum for $CoTPP(NO)_2$ in toluene solution (230 K): (a) (—) observed spectrum; (b) (---) computer simulation using $\langle g \rangle = 2.007$, $\langle A(^{59}Co) \rangle = 9.3$ G, $\langle A(^{14}N(NO)) \rangle = 4.15$ G, and $\langle A(^{14}N(por)) \rangle = 2.3$ G.

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Registry No. $RhOEP(O_2)$, 71986-22-6; $RhTPP(O_2)$, 71986-21-5; $RhOEP(O_2)(pip)$, 71986-20-4; $RhOEP((BuO)_3P)(O_2)$, 71986-19-1; $RhTPP(O_2)((EtO)_3P)$, 77944-58-2; RhTPP(Cl), 77944-60-6; RhTPP(NO), 77944-61-7; RhOEP(Cl), 36670-30-1; RhOEP(NO), 77944-62-8; $(RhOEP)_2$, 63439-10-1; $[RhOEP(NO)]^+$, 77944-63-9; RhOEP(NO)(Cl), 77944-64-0; RhOEP(H), 63372-77-0; H_2TPP, 917-23-7; H_2OEP, 2683-82-1; RhTPP(NO)(Cl), 77944-65-1; $RhOEP(NO)_2$, 77944-66-2; $RhTPP(NO)_2$, 77965-68-5.

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[21] B. B. Wayland and J. V. Minkiewicz, *J. Chem. Soc., Chem. Commun.*, 1016 (1976).