

When this ferric heme goes to high spin, an increase in the Fe-N(py) distances from 2.04 to 2.31 Å and an expansion of the porphyrin core by ~0.055 Å are observed. While a spin equilibrium analogous to that observed in this ferric heme is not significant in the ground state of hexacoordinate ferrous porphyrins, a spin change may be anticipated along the reaction coordinate for axial ligand dissociation for iron porphyrins when the trans ligand is a weak-field ligand. The intermediate may resemble those of high-spin pentacoordinate hemes such as that of Fe(TPP)(2-MeIm)<sup>20</sup> with the iron 0.42 Å out-of-plane.

When a strong-field ligand such as CO or BzNC is present, the iron will remain low spin with the intermediate resembling the structures of FeOEP(CS)<sup>21</sup> or FeTPP(NO)<sup>22</sup> with a smaller displacement (0.22 Å) from the N<sub>4</sub> plane and only slight increases in Fe-N<sub>4</sub> distances. Five-coordinate low-spin carbonyl and isocyanide heme derivatives have been observed in capped hemes,<sup>23,24</sup> providing convincing evidence that no spin change is expected for ligand dissociation trans to CO or BzNC. The trans ligand is thus much more inert than in a FeP(CH<sub>3</sub>Im)<sub>2</sub> complex, where a spin change is anticipated, giving a high-spin FeP(CH<sub>3</sub>Im). The FePc system is the only Fe macrocycle investigated to date that gives a more labile CH<sub>3</sub>Im in the FeN<sub>4</sub>(CH<sub>3</sub>Im)(BzNC) than in FeN<sub>4</sub>(CH<sub>3</sub>Im)<sub>2</sub>. This also suggests that the FePc(CH<sub>3</sub>Im) intermediate is low spin as indicated previously on the basis of the relative lability of CH<sub>3</sub>Im in FeP(CH<sub>3</sub>Im)<sub>2</sub> and FePc(CH<sub>3</sub>Im)<sub>2</sub>.

The spin anomalies present in the iron complexes are not possible in ruthenium systems. All RuN<sub>4</sub>L intermediates are expected to remain low spin, and thus, only the natural trans-labilizing effect of π-acceptor ligands is observed.

The proposed spin change along the reaction coordinate presents some theoretical difficulties which have been discussed for electron-transfer and photosubstitution reactions.<sup>25</sup> Spin

effects have not been seriously considered for thermal substitution reactions because higher electronic states are generally not thermally accessible, and one presumes that spin-forbidden processes are unimportant.

However, in substitution reactions of hemes and related systems, electronic states other than the ground state are known to be thermally accessible and the rates of intersystem crossing are rapid (despite being doubly spin forbidden). For Fe(II) complexes intersystem crossing rates of  $\geq 10^7$  s<sup>-1</sup> (<sup>1</sup>A  $\rightleftharpoons$  <sup>5</sup>T) are reported and furthermore the barriers for intersystem crossing seem to be primarily due to nonelectronic factors similar to those involved in ligand dissociation.<sup>25</sup> Estimated probabilities of <sup>1</sup>A  $\rightleftharpoons$  <sup>5</sup>T crossing in Fe(II) systems are  $\sim 10^{-3}$ .<sup>25</sup> One expects greater probabilities for the less spin-forbidden crossing to a triplet state involving population of d<sub>x<sup>2</sup>-y<sup>2</sup></sub>. Such a triplet state would have significantly weaker axial bonding but would not require the N<sub>4</sub> core expansion observed when d<sub>x<sup>2</sup>-y<sup>2</sup></sub> is populated. The triplet state involving d<sub>x<sup>2</sup>-y<sup>2</sup></sub> population has been proposed as the state responsible for the photolability of hemes.<sup>26</sup>

While alternative explanations may explain the unusual labilization and trans effects described here, it is difficult to account for the *magnitude* ( $\sim 10^6$ ) of these effects without invoking something dramatic like a spin change. Population of d<sub>x<sup>2</sup>-y<sup>2</sup></sub> will certainly profoundly assist axial ligand dissociation. Additional evidence for spin effects in thermal substitution reactions comes from studies of CO lability in Fe(14ane) and Fe(15ane) macrocycles.<sup>17</sup>

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**Registry No.** CO, 630-08-0; BzNC, 10340-91-7; RuPc(CO), 74891-28-4; RuTPP(BzNC)<sub>2</sub>, 81642-67-3; RuPc(BzNC)<sub>2</sub>, 83006-01-3; RuPc(BzNC)(CH<sub>3</sub>Im), 83006-02-4; RuPc(BzNC)(*t*-Bupy), 83006-03-5; CH<sub>3</sub>Im, 616-47-7; *t*-Bupy, 3978-81-2; RuOEP(BzNC)<sub>2</sub>, 83006-04-6; RuPc(CO)(CH<sub>3</sub>Im), 83006-05-7; RuPc(CO)(*t*-Bupy), 67588-49-2; RuPc, 27636-56-2.

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## Substituent Effects on the Redox Reactions of Para-Substituted Tetraphenylporphyrin Complexes of Ruthenium(II)

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The electrochemical oxidation and reduction of ((*p*-X)TPP)Ru(CO)(*t*-Bupy) were investigated in CH<sub>2</sub>Cl<sub>2</sub>-0.1 M TBAP solution. Six different complexes were investigated where X = Et<sub>2</sub>N, OMe, Me, Pr, Cl, and CF<sub>3</sub>. All of the complexes gave two oxidations and a single reduction process with the exception of ((*p*-Et<sub>2</sub>N)TPP)Ru(CO)(*t*-Bupy), which had three oxidations and one reduction. Plots of  $E_{1/2}$  vs.  $4\sigma$  were linear for the reduction and curvilinear for the first and second oxidation. Linear plots could be obtained for oxidations, however, when  $\sigma^+$  was utilized in place of  $\sigma$  as the substituent constant. The species produced upon the first controlled-potential oxidation were investigated by electronic absorption, ESR, and infrared spectroscopy, and on the basis of this data, the first oxidation was assigned as ring centered in all cases. Unlike previous results with [(*p*-X)TPP)Ru(CO)]<sup>+</sup>, a room-temperature ESR spectrum of [(*p*-Et<sub>2</sub>N)TPP)Ru(CO)(*t*-Bupy)]<sup>+</sup> could be obtained with  $g = 2.016$ . A mechanism for oxidation of all of the ((*p*-X)TPP)Ru(CO)(*t*-Bupy) complexes is presented, and comparisons are made with previously published data for ((*p*-X)TPP)Ru(CO) complexes in the same solvent.

### Introduction

The electrochemical oxidation of ruthenium(II) porphyrins such as (P)Ru(CO), (P)Ru(CO)(L), and (P)Ru(L)<sub>2</sub> has been well characterized in nonaqueous media.<sup>1-5</sup> When CO is one

of the extraplanar ligands, the site of oxidation is at the porphyrin ring, yielding a cation radical.<sup>1</sup> In contrast the

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Table I. Half-Wave Potentials (V vs. SCE) for ((p-X)TPP)Ru(CO)(t-Bupy) Complexes in CH<sub>2</sub>Cl<sub>2</sub>-0.1 M TBAP

substituent X	oxidn			redn		
	$E_{1/2}(1)$	$E_{1/2}(2)$	$E_{1/2}(3)$	$E_{1/2}(1)$	$4\sigma^a$	$4\sigma^+ a$
p-Et <sub>2</sub> N	0.50	0.73	1.06	-1.62	-2.80	-6.80 <sup>b</sup>
p-OMe	0.78	1.28		-1.56	-1.08	-3.12
p-Me	0.81	1.32		-1.54	-0.68	-1.24
p-Pr	0.85	1.33		-1.54	-0.60	-1.04
p-Cl	0.95	1.43		-1.46	0.92	0.44
p-CF <sub>3</sub>	1.04	1.47		-1.39	2.20	2.44

<sup>a</sup> Taken from ref 11. <sup>b</sup> Value presented is for p-Me<sub>2</sub>N substituent.

bis(pyridine) complex is oxidized at the central metal to yield a Ru(III) complex. The difference in potential between (TPP)Ru(CO) and (TPP)Ru(py)<sub>2</sub> is 600 mV in CH<sub>2</sub>Cl<sub>2</sub> with the bis(pyridine) complex being the most easily oxidized. Similar shifts of potential are seen on going from (TPP)Fe(CO) or (TPP)Os(CO) to the bis(pyridine) derivatives,<sup>6,7</sup> but in these cases the site of initial oxidation is invariably the metal center.

In a recent study Rillema et al.<sup>2</sup> investigated the redox reactions of ((p-X)TPP)Ru(CO) in CH<sub>2</sub>Cl<sub>2</sub>, where X was p-OCH<sub>3</sub>, p-CH<sub>3</sub>, p-F, p-Br, or p-Cl. In all cases the first oxidation was ring centered, similar to that of (TPP)Ru(CO), and potentials were related to the phenyl ring substituent. In this study we have reinvestigated these linear free energy relationships but have utilized a larger range of electron-donating and -withdrawing substituents. We have also extended the data set to include the electrochemical properties of ((p-Et<sub>2</sub>N)TPP)Ru(CO)(t-Bupy). This is the most basic ruthenium tetraphenylporphyrin ever investigated, and it was hoped that a clearer picture of the redox processes might be obtained by cathodically shifting the oxidation potentials into a region of greater potential stability. It was also our aim to try to shift the individual orbitals of the oxidation levels such that a third oxidation corresponding to the Ru(III) dication might be observed.

### Experimental Section

**Materials.** Synthesis of ((p-Et<sub>2</sub>N)TPP)Ru(CO) and ((p-Et<sub>2</sub>N)-TPP)Ru(CO)(t-Bupy) was according to the procedure of Eaton and Eaton.<sup>8</sup> Other samples of ((p-X)TPP)Ru(CO)(t-Bupy) including the above ligated complex were kindly provided by Drs. Sandra and Gareth Eaton. No difference in behavior was observed between the samples provided to us and those synthesized in our own laboratory. The supporting electrolyte, TBAP, was obtained from Eastman Chemical Co., recrystallized from ethyl acetate, and dried in vacuo prior to use. CH<sub>2</sub>Cl<sub>2</sub>, obtained from Fisher Scientific as technical grade, was twice distilled from P<sub>2</sub>O<sub>5</sub> and stored over 4-Å molecular sieves prior to use.

**Instrumentation.** Cyclic voltammetric measurements were made with use of the three-electrode system described in the literature.<sup>9</sup> Absorption spectra of the neutral and oxidized species were obtained with a Tracor Northern Rapid Scanning spectrometer by using thin-layer techniques or after generation in a coulometric cell to which was attached a spectrophotometric cell of path length 2 mm. ESR experiments were performed under a nitrogen atmosphere after exhaustive electrolysis on a Varian Model E-4 spectrometer. IR ex-

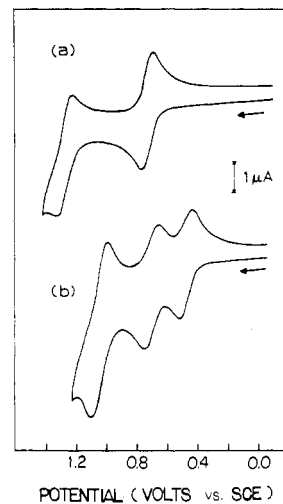


Figure 1. Cyclic voltammograms of equimolar (a) ((p-OMe)TPP)Ru(CO)(t-Bupy) and (b) ((p-Et<sub>2</sub>N)TPP)Ru(CO)(t-Bupy) in 0.1 M TBAP-CH<sub>2</sub>Cl<sub>2</sub> solution; scan rate 200 mV/s.

periments were performed on a Beckman 4250 infrared spectrophotometer, again after exhaustive electrolysis at each step.

### Results and Discussion

Cyclic voltammetry of ((p-Et<sub>2</sub>N)TPP)Ru(CO)(t-Bupy) at a Pt electrode in CH<sub>2</sub>Cl<sub>2</sub> reveals that the neutral species undergoes three reversible one-electron oxidations and a single reversible reduction. All electrode reactions were diffusion controlled. A theoretical value<sup>10</sup> of  $60 \pm 5$  mV was obtained for  $E_{pa} - E_{pc}$ . In addition, all peaks were approximately equal in height and  $E_p - E_{p/2}$  gave reversible separations of  $60 \pm 5$  mV. The oxidations of ((p-Et<sub>2</sub>N)TPP)Ru(CO)(t-Bupy) by cyclic voltammetry are shown in Figure 1b and the potentials listed in Table I. Also listed in this table are potentials for other complexes of ((p-X)TPP)Ru(CO)(t-Bupy) obtained under the same experimental conditions. As seen in this table, the potentials for ((p-Et<sub>2</sub>N)TPP)Ru(CO)(t-Bupy) are the most negative of those in the group and, in fact, are the most negative of any Ru(II) carbonyl porphyrin investigated to date. Also, of extreme importance is the fact that three, and not two, oxidations are observed. This has not been reported for any other ruthenium(II) porphyrin complex and is consistent with the ultimate formation of a Ru(III) dication after the global abstraction of three electrons.

Confirmation that each oxidation corresponds to a single-electron transfer and is not due to an equilibrium between two forms of the same oxidation state is given by controlled-potential electrolysis for each process. Data from this aspect of the study are summarized in Table II for both the oxidation and the reduction of ((p-Et<sub>2</sub>N)TPP)Ru(CO)(t-Bupy) and ((p-OMe)TPP)Ru(CO)(t-Bupy). This latter compound undergoes only two oxidations similar to all the other four Ru(II) complexes investigated.

Shifts in half-wave potentials such as that shown in Table I may be analyzed by one of the three linear free energy relationships<sup>11</sup> given by eq 1-3, where  $\sigma$ ,  $\sigma^+$ , and  $\sigma^-$  are the

$$\Delta E_{1/2} = 4\sigma\rho \quad (1)$$

$$\Delta E_{1/2} = 4\sigma^+\rho \quad (2)$$

$$\Delta E_{1/2} = 4\sigma^-\rho \quad (3)$$

substituent constants that measure the electron-donating or electron-withdrawing characteristic of the substituent and  $\rho$

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Table II. Stepwise Coulometric Measurements (faradays/mol) for Controlled-Potential Oxidation and Reduction of ((*p*-X)TPP)Ru(CO)(*t*-Bupy) in 0.1 M TBAP-CH<sub>2</sub>Cl<sub>2</sub> Solution<sup>a</sup>

compd	Red(1)	Ox(1) <sup>b</sup>	Ox(2) <sup>b</sup>	Ox(3) <sup>b</sup>
(( <i>p</i> -OMe)TPP)Ru(CO)( <i>t</i> -Bupy)	0.95 ± 0.09	0.97 ± 0.05	0.98 ± 0.05	<sup>c</sup>
(( <i>p</i> -Et <sub>2</sub> N)TPP)Ru(CO)( <i>t</i> -Bupy)	1.05 ± 0.07	0.99 ± 0.06	0.95 ± 0.05	1.03 ± 0.06

<sup>a</sup> All values represent the average of three measurements with the deviation given as the standard deviation (90% confidence limit) of the mean. <sup>b</sup> Oxidation values were obtained upon stepping from a potential anodic of each process to a value anodic of the following process. Potentials for these processes are seen in Table I and Figure 1. <sup>c</sup> No third oxidation observed.

Table III. Summary of Slopes ( $\rho$ ) and Correlation Coefficients ( $r$ ) for Analysis of the First Oxidation and First Reduction of ((*p*-X)TPP)Ru(CO) and ((*p*-X)TPP)Ru(CO)(*t*-Bupy)<sup>a</sup>

series	para substituents	type of $\sigma$	1st oxidn		1st redn	
			$\rho$	$r$	$\rho$	$r$
(( <i>p</i> -X)TPP)Ru(CO) <sup>b</sup>	OMe, Me, H, F, Cl, Br	$\sigma$	0.0637	0.96	0.0659	0.97
(( <i>p</i> -X)TPP)Ru(CO)( <i>t</i> -Bupy)	Et <sub>2</sub> N, OMe, Me, Pr, Cl, CF <sub>3</sub>	$\sigma$	0.104	0.95	0.047	0.99
		$\sigma^+$	0.057	0.99		
(( <i>p</i> -X)TPP)Ru(CO)( <i>t</i> -Bupy)	OMe, Me, Pr, Cl, CF <sub>3</sub>	$\sigma$	0.077	0.97	0.052	0.99
		$\sigma^+$	0.063	0.99		

<sup>a</sup> Data analyzed according to eq 1 and 2 by using the potentials and substituent constants listed in Table I. <sup>b</sup> Taken from data in ref 2.

is the reaction constant. The exact selection of  $\sigma$ ,  $\sigma^+$ , or  $\sigma^-$  will depend on the nature of the electrode reaction.

The values of  $\sigma^+$  or  $\sigma^-$  may be utilized for linear free energy relationships with electrode reactions when the reaction center is conjugated, but a simple criterion suggesting the proper selection of  $\sigma$  is not straightforward. For example, although it has been established that there is direct resonance conjugation between the porphyrin ring and the four phenyl groups of tetraphenylporphyrin,<sup>12,13</sup> values of  $\sigma^+$  or  $\sigma^-$  have generally not been utilized in past electrochemical studies of metalloporphyrins. In fact, all positive correlations with para- or meta-substituted tetraphenylporphyrins have utilized a simple  $\sigma$  value,<sup>14-20</sup> while only a single study of ring-substituted tetraphenylporphyrin complexes has involved correlations with  $\sigma^-$  and  $\sigma^+$ .<sup>21</sup>

For the specific compounds investigated in this study plots of  $E_{1/2}$  vs.  $4\sigma$  gave linear plots for reduction (correlation coefficient 0.99) with a slope of 0.047 V but curvilinear plots for the first (and possibly second) oxidation of ((*p*-X)TPP)Ru(CO)(*t*-Bupy). This is shown in Figure 2. In contrast, linear plots for the first oxidation were obtained (correlation coefficient 0.99) when  $4\sigma^+$  was utilized as the substituent constant for oxidations. This is shown in Figure 3. Also included in this plot are the data from Rillema et al.<sup>2</sup> for oxidation of ((*p*-X)TPP)Ru(CO) in CH<sub>2</sub>Cl<sub>2</sub>, containing 0.2 M [N(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>](PF<sub>6</sub>) as supporting electrolyte. The fact that their data are not superimposable with data from this study is not unexpected since different complexes were investigated (no sixth ligand was present in the initial study),<sup>22</sup> different supporting electrolytes were utilized, and the ionic strength

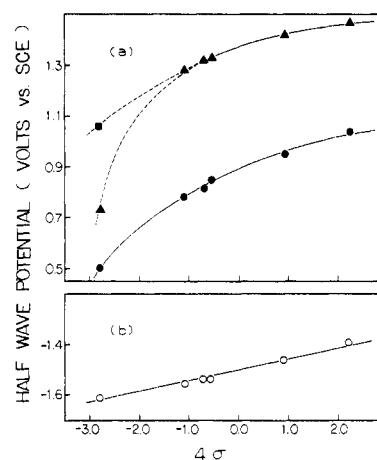


Figure 2. Plot of  $E_{1/2}$  vs.  $4\sigma$  for reactions of ((*p*-X)TPP)Ru(CO)(*t*-Bupy) in CH<sub>2</sub>Cl<sub>2</sub>-0.1 M TBAP solution: (a) first oxidation (●), second oxidation (▲), third oxidation (■); (b) first reduction (○).

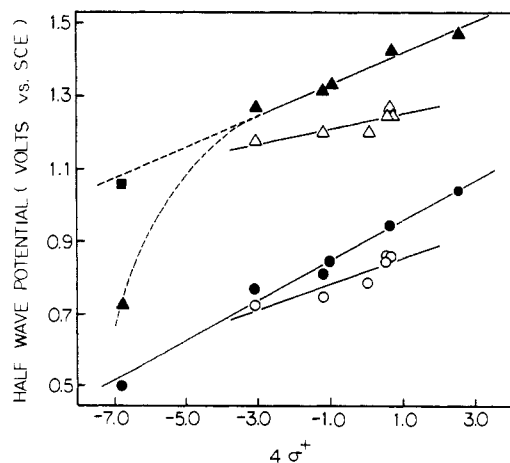


Figure 3. Plot of  $E_{1/2}$  vs.  $4\sigma^+$  for the following oxidations: ((*p*-X)TPP)Ru(CO)(*t*-Bupy) first oxidation (●), second oxidation (▲), third oxidation (■); ((*p*-X)TPP)Ru(CO) first oxidation (○), second oxidation (Δ). Data for the unligated compounds are taken from ref 2, and the substituent constant for *p*-Et<sub>2</sub>N is that for *p*-Me<sub>2</sub>N, which may be used interchangeably.

was different. What is important, however, is that both sets of data seem to fit the plot of  $E_{1/2}$  vs.  $4\sigma^+$  for the first oxidation. Analysis of the second oxidation in terms of  $\sigma$  or  $\sigma^+$  is less clear-cut due to the presence of a third wave with

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$((p\text{-Et}_2\text{N})\text{TPP})\text{Ru}(\text{CO})(t\text{-Bupy})$ , and for this reason correlations are shown with both dashed and solid lines (Figures 2a and 3).

A summary of the slopes and correlation coefficients for the first oxidation and first reduction of  $((p\text{-X})\text{TPP})\text{Ru}(\text{CO})(t\text{-Bupy})$  and  $((p\text{-X})\text{TPP})\text{Ru}(\text{CO})$  is given in Table III. All values of  $E_{1/2}$  were analyzed for correlations with  $\sigma$  while those specific for oxidations were also analyzed vs.  $\sigma^+$  and those for reductions vs.  $\sigma^-$ . None of the reductions gave a fit to plots of  $E_{1/2}$  vs.  $\sigma^-$  better than plots of  $E_{1/2}$  vs.  $\sigma$  ( $r = 0.97\text{--}0.99$ ). As seen from Table III, both series of compounds give a poor correlation with  $\sigma$ . In contrast, a good correlation with  $\sigma^+$  is obtained for the  $((p\text{-X})\text{TPP})\text{Ru}(\text{CO})(t\text{-Bupy})$  series ( $r = 0.99$ ).

A summary of substituent effects for the ring-centered reactions of eight different tetraphenylporphyrin complexes with  $\sigma$  as a substituent constant indicated that the average  $\rho$  for ring oxidation (to yield either cation radicals or dications) was  $0.07 \pm 0.01$  V.<sup>17</sup> A similar value of  $0.06 \pm 0.01$  V was reported for the first ring reduction to yield  $\pi$  anion radicals, and  $0.07 \pm 0.01$  V was reported for the second ring reduction to yield dianions. All plots were linear in these studies, and constancy of  $\rho$  over a wide range of central metal ions was accepted as a good indication that electron transfer involved the porphyrin ring and not the central metal ion. This criterion was utilized by Rillema and Meyer<sup>2</sup> to differentiate a ring- from a metal-centered reaction and to suggest the site of metal oxidation for complexes of  $((p\text{-X})\text{TPP})\text{Ru}(\text{CO})$ .

It is important to emphasize the values of  $\rho$  obtained by Rillema and Meyer<sup>2</sup> for the first oxidation (0.0659 V) and the first reduction (0.0637 V) are within experimental error of previously measured  $\rho$  values for other radical reactions of metalloporphyrins.<sup>14-19</sup> This suggests an interaction of the substituent with the porphyrin ring of  $((p\text{-X})\text{TPP})\text{Ru}(\text{CO})$  similar to that observed with other complexes of substituted tetraphenylporphyrins. However, as has been pointed out by Gross and co-workers,<sup>20,21</sup> the magnitude of  $\rho$  is small for the substituted tetraphenylporphyrins. Because of this, analysis of correlations between  $E_{1/2}$  and  $\sigma$ ,  $\sigma^-$ , or  $\sigma^+$  are best analyzed in terms of linearity of the plots in order to determine similarities or differences among a series of complexes. Linear plots imply the same mechanism throughout, while nonlinear plots imply a change of mechanism occurs as a function of the substituent. Deviation in a single point may also suggest a chemical or physical difference of this compound from that of the remaining series of compounds. For the specific porphyrins investigated, the curvilinear relationships in Figure 2a would seem to imply different mechanisms are occurring with complexes containing very electron-donating substituents. It might further be suggested that this change of mechanism is most extreme for the  $((p\text{-Et}_2\text{N})\text{TPP})\text{Ru}(\text{CO})(t\text{-Bupy})$  complex and that the first oxidation involves interaction of the ring and metal orbitals unlike the other complexes in the series. On the other hand, the linear relationship between  $E_{1/2}$  and  $\sigma^+$  for the first oxidation in Figure 3 and earlier characterizations of  $[((p\text{-X})\text{TPP})\text{Ru}(\text{CO})]^+ 1,2$  suggest a similar mechanism for the first oxidation of each complex in the  $((p\text{-X})\text{TPP})\text{Ru}(\text{CO})(t\text{-Bupy})$  series.<sup>24</sup>

Selection of the "correct" substituent constant for  $((p\text{-X})\text{TPP})\text{Ru}(\text{CO})(t\text{-Bupy})$  on the basis of data in the literature is not possible. Other linear free energy plots of  $((p\text{-X})\text{TPP})\text{Ru}(\text{CO})(t\text{-Bupy})$  which include the  $p\text{-Et}_2\text{N}$  substituent

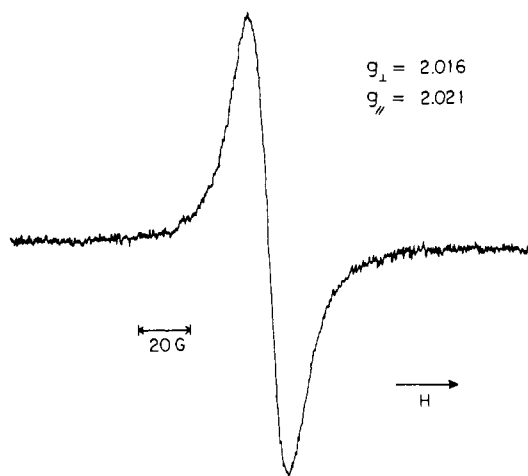


Figure 4. Room-temperature ESR spectra of  $((p\text{-Et}_2\text{N})\text{TPP})\text{Ru}(\text{CO})(t\text{-Bupy})$  after electrooxidation at 0.65 V in  $\text{CH}_2\text{Cl}_2\text{-}0.1$  M TBAP solution.

show linearity with  $\sigma$  for ligand exchange<sup>8</sup> but curvilinearity for ring rotation.<sup>25,26</sup> Clearly the  $\text{Et}_2\text{N}$  substituent affects the specific reactions differently, and specific information is needed on the electrode reactions of each compound in the series.

In order to determine the type of reaction (ring or metal centered), we carried out controlled-potential electrolysis for each oxidation and investigated the product by electronic absorption, infrared, and ESR spectroscopy. Before electrolysis no ESR signal was observed for  $((p\text{-Et}_2\text{N})\text{TPP})\text{Ru}(\text{CO})(t\text{-Bupy})$ . After electrolysis at 0.83 and 1.20 V no signal was observed. However, after electrolysis at 0.65 V, the ESR signal of  $[((p\text{-Et}_2\text{N})\text{TPP})\text{Ru}(\text{CO})(t\text{-Bupy})]^+$  shown in Figure 4 was obtained. This spectra was obtained at 293 K. Spectra were also obtained at 77 K. The observed  $g = 2.016$  is characteristic of oxidation at the porphyrin ring to form the cation radical<sup>27,28</sup> and is similar to the  $g = 2.004$  obtained for  $[(\text{TPP})\text{Ru}(\text{CO})(\text{py})]^+ 2$ . It is especially interesting to note that other Ru(II) porphyrin radicals do not exhibit signals at room temperature.<sup>1,2</sup> The lack of an ESR signal from the species generated at 0.83 and 1.20 V is noninformative. The difficulty in obtaining Ru(III) ESR spectra has been discussed by Goodman and Raynor,<sup>29</sup> but ESR spectra of other Ru(III) complexes have been reported.<sup>30</sup>

Infrared spectra obtained under the same conditions as the ESR spectra also support the assignment of  $\pi$ -radical formation on the first oxidation. The singly oxidized complex has a band at  $1245\text{ cm}^{-1}$ , which was not present for the neutral complex. This is slightly outside the range of  $1270\text{--}1295\text{ cm}^{-1}$  diagnostic of a radical cation.<sup>31</sup> More importantly, however, the  $\nu(\text{CO})$  band for the singly oxidized species is found at  $1960\text{ cm}^{-1}$ . This shift is only  $25\text{ cm}^{-1}$  from that of the neutral complex, which has  $\nu(\text{CO})$  at  $1935\text{ cm}^{-1}$ , and is in agreement with shifts of  $15\text{--}33\text{ cm}^{-1}$  upon formation of other Ru(II) cation radicals.<sup>1</sup> Finally, the electronic absorption spectra of  $[((p\text{-Et}_2\text{N})\text{TPP})\text{Ru}(\text{CO})(t\text{-Bupy})]^+$  are shown in Figure 5. During the electrolysis at 0.65 V the Soret peak at  $435.7\text{ nm}$  as well as peaks at  $543.2$  and  $584.8\text{ nm}$  decrease. At the same

(24) In light of this linear plot we have begun to reanalyze all earlier data on porphyrin oxidation potentials. It now appears likely that better correlations for oxidation are obtained between  $E_{1/2}$  and  $\sigma^+$  than between  $E_{1/2}$  and  $\sigma$ . This was not recognized earlier due to the small range of substituents utilized and does not become readily discernible unless compounds with a larger range of electron-donating and electron-withdrawing substituents are investigated.

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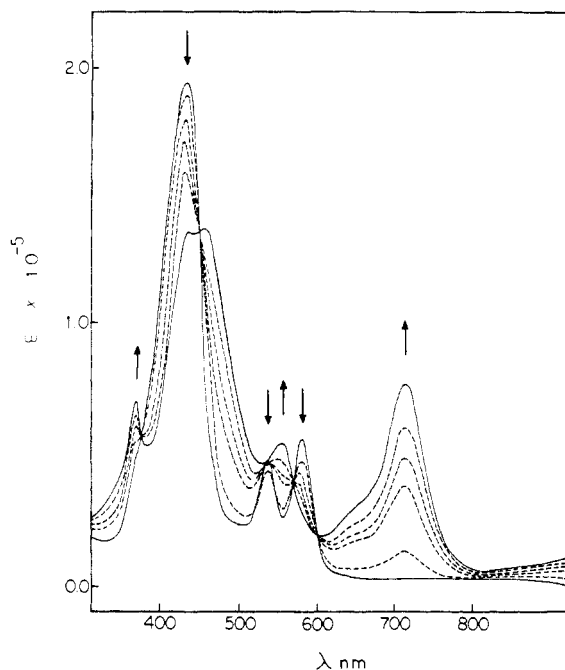
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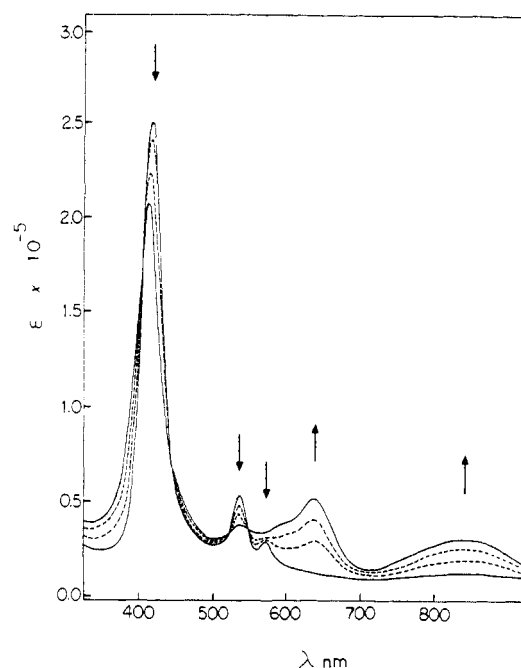


**Figure 5.** Time-resolved electronic absorption spectra obtained at 0.65 V for the reaction  $[(p\text{-Et}_2\text{N})\text{TPP}]\text{Ru}^{\text{II}}(\text{CO})(t\text{-Bupy}) \rightleftharpoons [(p\text{-Et}_2\text{N})\text{TPP}]\text{Ru}^{\text{II}}(\text{CO})(t\text{-Bupy})^+ + e^-$ .

time a new peak at 709.5 nm appears, which is characteristic of porphyrin ring oxidation to yield a cation radical.<sup>27,28</sup> This spectrum could be reversibly returned to that of the starting species upon rereduction at 0.0 V, and clear isosbestic points were observed for the transition. The oxidized species had a half-life of approximately 7 h at open circuit. In contrast, the species generated by the second and the third oxidation were not stable on the time scale of the spectroelectrochemical experiment. A new species was generated on the first step that had some spectral characteristics of a dication, but cyclic voltammetry of this solution showed the new species to be electroinactive.

For comparison, the spectroelectrochemistry of  $(p\text{-OMe})\text{TPP}]\text{Ru}(\text{CO})(t\text{-Bupy})$  was also done. During the first oxidation at 1.0 V the spectra changed in a way similar to that observed during the first stage of  $(p\text{-Et}_2\text{N})\text{TPP}]\text{Ru}(\text{CO})(t\text{-Bupy})$  oxidation; i.e., the Soret peak at 415.6 nm decreased and shifted to shorter wavelengths while the two metalloporphyrin bands at 535 and 571.4 nm also decreased. New peaks were observed at 636 and 839.8 nm characteristic of cation radicals. This is shown in Figure 6. After electrolysis at 1.4 V those peaks disappeared, and a new spectrum was obtained which might be characterized as that of a dication. Again, however, the stability of this species was small and the exact identity of the initially produced species is questionable.

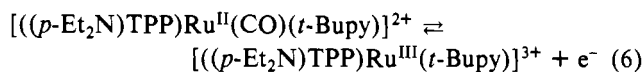
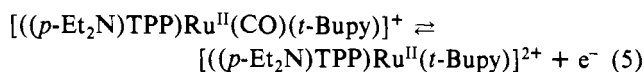
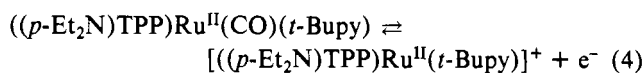
On the basis of the IR, ESR, and electronic absorption spectra there is no doubt that the first oxidation for all complexes investigated in this study is at the  $\pi$  ring system. Analysis of the second oxidation is less clear-cut. Rillema et al.<sup>2</sup> have assigned the second oxidation as due to the transition  $\text{Ru}(\text{II}) \rightleftharpoons \text{Ru}(\text{III})$ . This assignment was based on the potential separation of the first and the second wave, which was larger than that generally observed for successive cation radical and dication formation, as well as the magnitude of  $\rho$  in the  $E_{1/2}$  vs.  $\sigma$  plots. There is some merit to the first argument, which has been used extensively in the past,<sup>28,32-34</sup> although there are



**Figure 6.** Time-resolved electronic absorption spectra obtained at 1.0 V for the reaction  $[(p\text{-OMe})\text{TPP}]\text{Ru}^{\text{II}}(\text{CO})(t\text{-Bupy}) \rightleftharpoons [(p\text{-OMe})\text{TPP}]\text{Ru}^{\text{II}}(\text{CO})(t\text{-Bupy})^+ + e^-$ .

some exceptions in the literature, especially with complexes containing non transition metals such as Zn and Cd.<sup>35</sup> The argument regarding the magnitude of  $\rho$  and the site of oxidation is also generally true<sup>15-18,20</sup> although the exact magnitude of the differences expected is unclear at this time.

In summary, we cannot elucidate the mechanism for all oxidations observed in this study. We would like to suggest, however, that the reaction sequence for  $(p\text{-Et}_2\text{N})\text{TPP}]\text{Ru}(\text{CO})(t\text{-Bupy})$  oxidation is as given by eq 4-6. Rationale for



our assignment is based on the 230-mV difference between the first and second oxidation (see Table I) and the fact that linear relationships with  $\sigma^+$  are observed for the first and third oxidations of the  $(p\text{-Et}_2\text{N})\text{TPP}]\text{Ru}(\text{CO})(t\text{-Bupy})$  complex and the remainder of the complexes in the series which have previously been assigned as ring- and metal-centered reactions, respectively.<sup>2</sup> The suggestion that dication formation (reaction 5) occurs *before* metal oxidation (reaction 6) as has been suggested with the other complexes in this series would imply a metal-ligand crossover due to the difference in substituent effects on each reaction site. This has previously been observed for the reactions of  $(p\text{-X})\text{TPP}]\text{Ni}$  in  $\text{CH}_2\text{Cl}_2$ .<sup>18</sup> Attempts to locate a third oxidation for any of the other  $\text{Ru}(\text{II})$  complexes were unsuccessful in all electrochemical solvents investigated. However, it is hoped that the use of axial ligands which donate substantial electron density to the metal might be successful in shifting oxidation potentials such that these oxidations may be obtained for other  $\text{Ru}(\text{II})$  complexes at potentials more

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negative than the anodic limit of our solvent. These studies are presently under way.

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acknowledged.

**Registry No.** ((*p*-Et<sub>2</sub>N)TPP)Ru(CO)(*t*-Bupy), 60860-92-6; ((*p*-OMe)TPP)Ru(CO)(*t*-Bupy), 60882-60-2; ((*p*-Me)TPP)Ru(CO)(*t*-Bupy), 60909-08-2; ((*p*-*i*-Pr)TPP)Ru(CO)(*t*-Bupy), 34714-21-1; ((*p*-Cl)TPP)Ru(CO)(*t*-Bupy), 60840-42-8; ((*p*-CF<sub>3</sub>)TPP)Ru(CO)(*t*-Bupy), 60840 41-7; [((*p*-Et<sub>2</sub>N)TPP)Ru<sup>II</sup>(CO)(*t*-Bupy)]<sup>+</sup>, 83006-29-5; [((*p*-OMe)TPP)Ru<sup>II</sup>(CO)(*t*-Bupy)]<sup>+</sup>, 83006-30-8.

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## Bis-tren Cryptates of Cobalt(II), Nickel(II), Copper(II), and Zinc(II). Protonation Constants, Formation Constants, and Hydroxo Bridging

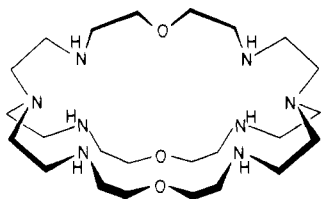
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Potentiometric equilibrium measurements of hydrogen ion concentration have been employed for the determination of protonation constants of the macrobicyclic ligand bis-tren at 25 °C in solutions maintained at 0.10 M ionic strength with potassium nitrate, sodium perchlorate, potassium chloride, and the sodium salt of 2,4,6-trimethylbenzenesulfonic acid as supporting electrolytes. The protonation constants were found to be dependent on the nature of the supporting electrolyte, with sodium perchlorate and sodium trimethylbenzenesulfonate having considerably less interaction with the ligand than potassium nitrate and potassium chloride. These results are interpreted in terms of nitrate and chloride binding to the protonated ligand. With the divalent metal ions, bis-tren forms in each case mononuclear and dinuclear inclusion complexes of the cryptate type, as well as a series of protonated and hydroxo derivatives. The mononuclear complexes are less stable than those of tren itself and yield protonated forms. The binding of the second cation is weaker than that of the first. It gives dinuclear cryptates which further take up anions, forming cascade type complexes. Thus, the cryptate structure stabilizes bridging of the two bound metal ions by one or two hydroxo groups. The dinuclear Co(II) complex was found to combine reversibly with dioxygen, forming a doubly bridged species containing both hydroxo and peroxy bridges within the cryptate structure.

### Introduction

Macropolycyclic ligands containing two binding subunits are able to form dinuclear cryptates by inclusion of two metal cations into the molecular cavity and may further bind substrate species held by the cation centers, yielding cascade complexes.<sup>2</sup> Such is the case, in particular, with the bis-tren cryptand **1**, a macrobicyclic system that was found to complex



**1**, schematic representation of bis-tren free base

two cations by its two tren (2,2',2''-tri-aminotriethylamine) type subunits, forming dinuclear cation cryptates of the axial macrobicyclic type.<sup>2a</sup> The synthesis of **1** and its complexation with a number of transition-metal cations have been reported earlier.<sup>2b</sup> The hexaprotonated form of bis-tren was found to bind selectively a number of anions presumably by hydrogen bonding with the protonated nitrogen sites and inclusion into the molecular cavity, yielding anion cryptates.<sup>3</sup> We now

report potentiometric studies on the formation of mono- and dinuclear cryptates between **1** and Co(II), Ni(II), Cu(II), and Zn(II) cations, as well as bridged cascade type species.

### Experimental Section

**Materials.** Bis-tren (7,19,30-trioxa-1,4,10,13,16,22,27,33-octaazabicyclo[11.11.11]pentatriacontane) was synthesized by the method previously described.<sup>2b</sup> In this work two samples were employed, a 0.10-g sample of the crystalline perchlorate and a 0.100-g sample of the free base. Since the latter is hygroscopic, the stock solution required standardization by potentiometric titration. Stock solutions (0.0200 M) of reagent grade metal nitrates were prepared in doubly distilled water, and their exact concentrations were determined by direct potentiometric titration with standard EDTA<sup>4</sup> in the presence of appropriate indicators. A carbonate-free solution of 0.1000 M potassium hydroxide was prepared from Dilut-it ampules and standardized with potassium acid phthalate. The supporting electrolytes potassium nitrate, potassium chloride, and sodium perchlorate were also obtained as reagent grade materials. The sample of tren employed for comparison with bis-tren was commercial grade material that was further purified by fractional distillation and successive recrystallizations from hydrochloric acid. The sodium 2,4,6-trimethylbenzenesulfonate used as a supporting electrolyte was prepared by sulfonation of 1,3,5-trimethylbenzene and was purified by successive recrystallizations from water-ethanol mixtures.

**Procedures.** The potentiometric equilibrium measurements of tren and bis-tren in the absence and in the presence of metal ions were carried out with a Beckman Research pH meter fitted with blue-glass and calomel reference electrodes and calibrated to read  $-\log [H^+]$  directly. The temperature was maintained at  $25.00 \pm 0.05$  °C, and the ionic strength was adjusted to 0.100 M by the addition of the

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