$[(TPP)Ru(CO)(py)]^+$ as compared to (TPP)Ru(CO) over $[(TPP)Ru(CO)]^+$.

It should be noted, however, that the 100-mV difference in potential refers to differences between neat solvents and that addition of smaller quantities of pyridine to CH_2Cl_2 or $EtCl_2$ (which forms (TPP)Ru(CO)(py)) produced only slight shifts of potential from those of the five-coordinate species. This is shown clearly in Figure 7, which illustrates half-wave potentials monitored during the titration of (TPP)Ru(CO) with py in CH_2Cl_2–0.1 M TBAP.

There is no significance to the slope $\Delta E_{1/2}/\Delta \log (py)$ between log [py] = −6 and −2, and this only indicates a transition region upon pyridine binding. The flat region above 10^{-2} M py, however, indicates that py is not lost upon oxidation of (TPP)Ru(CO)(py). If a loss of ligand occurred in this region, a predicted 60 mV/log [L] slope would be obtained. The 30-mV difference in potentials between (TPP)Ru(CO) and (TPP)Ru(CO)(py) half-wave potentials reflects the almost identical stability constants of (TPP)Ru(CO)(py) and $[(TPP)Ru(CO)(py)]^+$. In fact, calculation of log β_1 for the addition of py to $[(TPP)Ru(CO)]^+$ using the data in this figure and equations derived in previous publications[36,37] leads to a value of log $\beta_1^+ = 4.10$ for reaction 2.[38] This value may be

$$[(TPP)Ru(CO)]^+ + py \rightleftarrows [(TPP)Ru(CO)(py)]^+ \quad (2)$$

compared to a log $\beta_1 = 4.63$ for addition of pyridine to the neutral complex according to eq 1.[38]

In summary, we have shown that solvent molecules will strongly bind to (TPP)Ru(CO) at the single vacant axial position to form (TPP)Ru(CO)(S) and that, upon oxidation or reduction of this species, a six-coordinate anion or cation radical of Ru(II) may be produced. We have also measured the first stability constants for ligand addition to (TPP)Ru(CO) and shown that the magnitude of this constant is directly related to the Gutmann donor number of the solvent. Finally, we have measured, for the first time, a formation constant for addition of a donor ligand to $[(TPP)Ru(CO)]^+$. This aspect of the study is most important in attempting to "tune" redox potentials of these types of systems, where it is possible to convert between a metal-centered and a ring-centered oxidation as a function of the bound axial ligand. This will be the subject of a future communication.

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Registry No. (TPP)Ru(CO), 32073-84-0; (TPP)Ru(CO)(CH_3NO_2), 82614-53-7; (TPP)Ru(CO)(C_6H_5CN), 82614-54-8; (TPP)Ru(CO)(CH_3CN), 82621-16-7; (TPP)Ru(CO)(*n*-PrCN), 82614-55-9; (TPP)Ru(CO)($(CH_3)_2CO$), 82614-56-0; (TPP)Ru(CO)(THF), 82614-57-1; (TPP)Ru(CO)(DMF), 82614-58-2; (TPP)Ru(CO)(DMA), 82614-59-3; (TPP)Ru(CO)(Me_2SO), 82621-20-3; (TPP)Ru(CO)(py), 41751-82-0; $(TPP)Ru(CO)(CH_3NO_2)^+$, 82614-60-6; $(TPP)Ru(CO)(C_6H_5CN)^+$, 82614-61-7; $(TPP)Ru(CO)(CH_3CN)^+$, 82614-62-8; $(TPP)Ru(CO)(n\text{-}PrCN)^+$, 82614-63-9; $(TPP)Ru(CO)((CH_3)_2CO)^+$, 82614-64-0; $(TPP)Ru(CO)(THF)^+$, 82614-65-1; $(TPP)Ru(CO)(DMF)^+$, 82614-66-2; $(TPP)Ru(CO)(DMA)^+$, 82614-67-3; $(TPP)Ru(CO)(Me_2SO)^+$, 82614-68-4; $(TPP)Ru(CO)(py)^+$, 43070-17-3; $(TPP)Ru(CO)(C_6H_5CN)^-$, 82614-69-5; $(TPP)Ru(CO)(CH_3CN)^-$, 82614-70-8; $(TPP)Ru(CO)(n\text{-}PrCN)^-$, 82614-71-9; $(TPP)Ru(CO)((CH_3)_2CO)^-$, 82614-72-0; $(TPP)Ru(CO)(THF)^-$, 82614-73-1; $(TPP)Ru(CO)(DMF)^-$, 82614-74-2; $(TPP)Ru(CO)(DMA)^-$, 82614-75-3; $(TPP)Ru(CO)(Me_2SO)^-$, 82614-76-4; $(TPP)Ru(CO)(py)^-$, 82621-21-4.

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Investigation of the Electrochemical Reactivity and Axial Ligand Binding Reactions of Tetraphenylporphyrin Carbonyl Complexes of Ruthenium(II)

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Stability constants for nitrogenous base addition to (TPP)Ru(CO) and $[(TPP)Ru(CO)]^+$ were calculated. Spectrophotometric methods were utilized for stability constant determinations of the five-coordinate neutral complex while a combination of spectrophotometric and electrochemical techniques was utilized to calculate values for ligand addition to the cation radical. Twenty different nitrogenous bases were investigated. For (TPP)Ru(CO)(L) values of log β_1 ranged from 3.62 to 5.63 and generally increased as a function of the ligand pK_a. Values of log β_1 for formation of $[(TPP)Ru(CO)(L)]^+$ ranged from 2.40 to 6.63 and also increased with the ligand pK_a. Comparisons were made between the measured values of log β_1 and reversible potentials for the electrode reaction $(TPP)Ru(CO)(L) \rightleftarrows [(TPP)Ru(CO)(L)]^+$.

Introduction

The electrochemical oxidation of ruthenium(II) porphyrins such as (P)Ru(CO), (P)Ru(CO)(L), and $(P)Ru(L)_2$ has been reported in nonaqueous media where P = OEP^{2-}, $Etio^{2-}$, and TPP^{2-} and L = py, CH_3CN, and THF.[1,2] When CO is one of the extraplanar ligands, the initial site of oxidation is at the conjugated porphyrin ring, yielding a π cation radical. In contrast, when ruthenium(II) is decarbonylated, the site of initial oxidation is at the central metal ion, yielding the corresponding Ru(III) complex.[1,2] The difference in potentials between these two reactions is approximately 600 mV with the decarbonylated complex being the most easily oxidized. For example, $(TPP)Ru(py)_2$ is oxidized to $[(TPP)Ru^{III}(py)_2]^+$ at 0.21 V in CH_2Cl_2 while $[(TPP)Ru^{II}(CO)(py)]^+$ is produced from (TPP)Ru(CO)(py) at 0.81 V in the same solvent. Both the carbonyl and non-carbonyl complexes undergo a second oxidation at potentials greater than 1.1 V, with the product of $[(TPP)Ru^{II}(CO)(py)]^+$ oxidations being assigned as abstraction from the metal center.[3]

This example of how axially coordinated ligands can change not only the half-wave potentials but also the site of porphyrin oxidation is remarkable and is clearly related to the stabilizing

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of Ru(II) by the carbonyl ligand. However, very little information exists on how trans ligands other than pyridine in (P)Ru(CO)(L) affect the change in redox potentials and, at the same time, the site of oxidation for the reaction (P)Ru(CO)(L) $\rightleftarrows$ $[(P)Ru(CO)(L)]^+$.

For some years our laboratory has been investigating how changes in porphyrin structures and axially coordinated ligands modify the redox properties of the central metalloporphyrin ion as well as the π ring system. Our interest in this study was to investigate the redox potentials of (TPP)Ru(CO)(L) as a function of changes in the axial ligand, L, and at the same time to relate any changes in potential to changes in formation constants for addition of the sixth axial ligand to the oxidized and reduced form of the complex. The ligand-addition reactions were investigated in CH_2Cl_2 containing 0.1 M TBAP and are represented as shown in eq 1 and 2. Similar investigations of reaction 1 have already been carried out for reactions of (TPP)Ru(CO) with 10 different bonding solvents utilized as ligands in CH_2Cl_2.[4]

$$\text{(TPP)Ru(CO)} + \text{L} \rightleftarrows \text{(TPP)Ru(CO)(L)} \qquad (1)$$

$$[\text{(TPP)Ru(CO)}]^+ + \text{L} \rightleftarrows [\text{(TPP)Ru(CO)(L)}]^+ \qquad (2)$$

In this present paper, L is one of 20 different substituted pyridines or imidazoles that vary in ligand pK_a between 0.67 and 11.10 (the ligand pK_a is defined as the pK_a value of the ligand conjugate acid in water, pK_{BH^+}). There are presently no values in the literature for reaction 1 or 2 with nitrogenous base donor atoms. Thus, determinations of log β_1 presented in this study represent the first values for formation of the mixed CO–nitrogenous base complex.

Experimental Section

Chemicals. Synthesis of (TPP)Ru(CO) was according to the procedure of Rillema et al.,[3] who used a modification of the method of Tsutsui et al.[5,6] The visible spectrum of the starting material, (TPP)Ru(CO), was consistent with previously reported literature values. Reagent grade CH_2Cl_2, which was used as a solvent, was distilled from P_2O_5 and stored over 4-Å Linde molecular sieves prior to use. Twenty different nitrogenous ligands were used in this study and were obtained from Aldrich Chemical Co. These were purified by standard literature methods. The supporting electrolyte, TBAP, was obtained from Eastman Chemical Co., recrystallized from ethyl acetate, and dried in vacuo prior to use.

Instrumentation. Cyclic voltammetric measurements were made by using a three-electrode system and a Princeton Applied Research Model 174A polarographic analyzer. A platinum button served as the working electrode with a platinum wire as the counterelectrode. A saturated calomel electrode (SCE), separated from the bulk of the solution by a fritted glass disk, was used as the reference electrode. Current–voltage curves were collected on a Houston Instruments Omnigraphic X-Y recorder at scan rates of 0.020 to 0.200 V/s. All absorption spectra were obtained at 20.0 ± 0.5 °C with a Cary Model 14 spectrophotometer using a cell of path length 1.0 cm.

Calculation of Stability Constants. Stability constants for addition of each nitrogenous base to (TPP)Ru(CO) in CH_2Cl_2 with 0.1 M TBAP were calculated spectrophotometrically by the computer program SQUAD.[7] The concentrations of porphyrin and TBAP were kept constant at 5×10^{-5} and 0.1 M, respectively, and the ligand concentration varied from 0 to 5×10^{-4} M. Each ligand was titrated three times. For each titration, 14 different spectra were obtained. From each spectrum, 24 absorbances were taken between 510.0 and 567.5 nm at 2.5-nm intervals.

Stability constants (log β_1^+) for the complexation of the $[(TPP)Ru(CO)]^+$ radical cation with nitrogenous bases were determined by monitoring the shifts in $E_{1/2}$ as a function of free ligand concentration, [L]. Plots of $E_{1/2}$ vs. log [L] were constructed, and from the slope of the plots, the change in axial ligand coordination number was determined by eq 3, where $(E_{1/2})_c$ and $(E_{1/2})_s$ are the half-wave potentials of the complexed species and uncomplexed species, respectively, [L] is the free-ligand concentration, n is the number of electrons transferred in the diffusion-controlled reaction, and p and q are the number of ligands bound to the cation radical and neutral species, respectively. For each ligand, log β_1^0 was determined spectrophotometrically and combined with the electrochemical data to calculate values for log β_1^+ at 1 M ligand concentration. Further details on the method of calculation for the case of metalloporphyrin reactions have been presented in previous publications.[8-10]

$$(E_{1/2})_c = (E_{1/2})_s - 0.059 \log (\beta_1^+/\beta_1^0) - 0.059 \log [\text{L}]^{p-q} \quad (3)$$

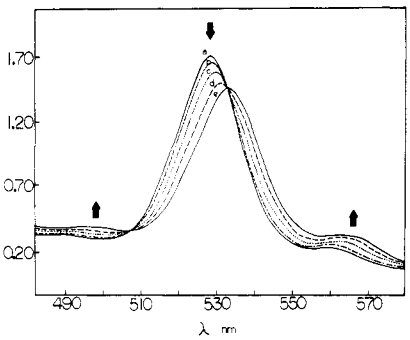

Figure 1. Spectra obtained during titration of 5×10^{-5} M (TPP)Ru(CO) with imidazole in CH_2Cl_2 with 0.1 M TBAP. The concentration of imidazole is as follows: (a) 0 M; (b) 2×10^{-7} M; (c) 5×10^{-6} M; (d) 3×10^{-5} M; (e) 5×10^{-5} M.

Table I. Absorption Maxima (nm) and Molar Absorptivities of (TPP)Ru(CO) and Pyridinate Complexes in CH_2Cl_2 with 0.1 M TBAP

		λ_{max}, nm			$10^{-4}\epsilon$		
no.	ligand	Soret	β	α	Soret	β	α
	none	411	528	560	20.9	1.70	0.24
1	3,5-dichloropyridine	411	531	564	21.4	1.35	0.31
2	3-cyanopyridine	411	531	564	21.5	1.36	0.29
3	4-cyanopyridine	412	531	564	21.5	1.36	0.29
4	3-chloropyridine	412	532	565	21.6	1.37	0.31
5	3-bromopyridine	412	532	565	21.9	1.35	0.29
6	3-acetylpyridine	412	532	565	21.8	1.36	0.30
7	4-acetylpyridine	412	533	566	21.7	1.34	0.30
8	pyridine	413	533	566	22.5	1.35	0.32
9	3-picoline	413	533	566	22.6	1.36	0.31
10	2-picoline	413	531	564	22.2	1.63	0.28
11	4-picoline	413	533	566	23.1	1.35	0.33
12	3,4-lutidine	413	533	567	23.0	1.36	0.33
13	2-aminopyridine	413	531	564	20.7	1.60	0.29
14	4-aminopyridine	413	534	567	23.8	1.38	0.34
15	4-(*N*,*N*-dimethylamino)-pyridine	413	534	568	23.9	1.39	0.36
16	piperidine	413	535	568	23.5	1.44	0.35
17	imidazole	413	534	568	23.2	1.35	0.38
18	1-methylimidazole	413	534	568	23.5	1.32	0.35
19	2-methylimidazole	413	534	568	23.0	1.21	0.34
20	1,2-dimethylimidazole	413	534	568	23.1	1.30	0.37

Results and Discussion

Ligand Addition to (TPP)Ru(CO) and $[(TPP)Ru(CO)(L)]^+$. In the absence of coordinating ligand, the normal (TPP)Ru(CO) absorption spectrum in CH_2Cl_2 and 0.1 M TBAP has a Soret band at λ_{max} = 411 nm, two weaker bands at λ_{max} = 560 nm and 528 nm, and a shoulder at λ_{max} = 490 nm. Additions of nitrogenous bases to CH_2Cl_2 solutions of (TPP)-

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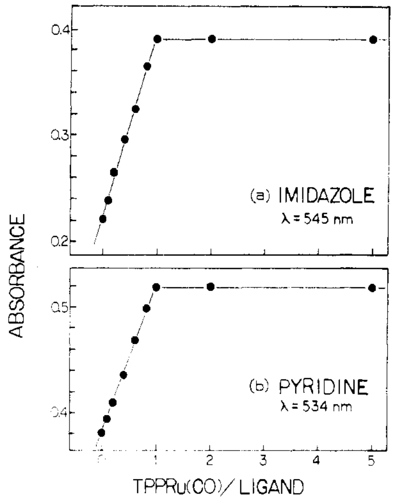

Figure 2. Mole ratio plots of absorbance vs. the ratio of (TPP)Ru(CO) to ligand when the ligand is (a) imidazole or (b) pyridine in CH_2Cl_2 with 0.1 M TBAP.

Ru(CO) produced a small red shift of all peaks and a change in the relative molar absorptivities of the α and β peaks. This is shown in Figure 1 for the titration of (TPP)Ru(CO) with imidazole.

All nitrogenous bases studied in this work showed similar spectral changes upon complexation with (TPP)Ru(CO). The absorption maxima and molar absorptivities of these (TPP)Ru(CO)(L) complexes in CH_2Cl_2 with 0.1 M TBAP are listed in Table I. As seen from this table, total spectral shifts upon complexation of (TPP)Ru(CO) were small, ranging from 3 to 4 nm for 3,5-dichloropyridine (**1**) to 7 to 8 nm for piperidine (**16**). The presence of isosbestic points (at λ = 508 and 534 nm for L = imidazole, Figure 1) clearly indicates the presence of only two species in solution.

Mole ratio plots were constructed of absorbance vs. the ratio of (TPP)Ru(CO) to ligand. All plots gave sharp breaks at the ratio of porphyrin to ligand of 1:1. An example is given in Figure 2 for complexation with imidazole and with pyridine. The lack of spectral change after a 1:1 porphyrin to ligand ratio indicates that the pyridine strongly complexes with (TPP)Ru(CO) at the sixth vacant site and that a rather large stability constant can be expected.

Calculated values of log β_1^0 for reaction 1 and their standard deviations obtained in this study from SQUAD are summarized in Table II. The 20 different ligands investigated can be divided into three groups: nonsterically hindered pyridines (**1–9**, **11**, **12**, **14–16**), nonsterically hindered imidazoles (**17**, **18**), and sterically hindered pyridines and imidazoles (**10**, **13**, **19**, **20**). The range of stability constants is quite small and only slightly increases as the pK_a of the axial ligand increases. Also, the range of log β_1^0 for ligands **17–20** is virtually identical with values obtained for addition of the same ligands to (TPP)Zn (log β_1^0 = 5.11–5.47),[8] (TPP)Mg (log β_1^0 = 4.98–5.76),[11] and (TPP)Cd (log β_1^0 = 4.23–5.59).[12,13]

After ascertaining that each of the 20 ligands would complex with (TPP)Ru(CO), cyclic voltammograms were obtained in the presence and absence of each complexing donor ligand. In CH_2Cl_2 with 0.1 M TBAP containing no ligand, half-wave potentials of 0.85 and 1.26 V were obtained in agreement with literature values.[2,3] Increasing concentrations of ligand were then added to solution, and the potential was recorded after each addition.

Table II. Formation Constants for Ligand Addition

no.	ligand	pK_{BH^+} [a]	log β_1^0 [b]	log β_1^+ [c]
1	3,5-dichloropyridine	0.67	4.11 ± 0.01	2.40
2	3-cyanopyridine	1.45	4.16 ± 0.03	2.84
3	4-cyanopyridine	1.86	4.22 ± 0.06	2.97
4	3-chloropyridine	2.81	4.26 ± 0.02	3.16
5	3-bromopyridine	2.84	4.39 ± 0.01	3.31
6	3-acetylpyridine	3.18	4.45 ± 0.01	3.59
7	4-acetylpyridine	3.51	4.52 ± 0.01	3.81
8	pyridine	5.29	4.63 ± 0.01	4.10
9	3-picoline	5.79	4.67 ± 0.04	4.36
10	2-picoline	5.96	3.62 ± 0.07	3.52
11	4-picoline	5.98	4.80 ± 0.03	4.51
12	3,4-lutidine	6.46	4.88 ± 0.02	4.85
13	2-aminopyridine	6.82	3.92 ± 0.03	N.R.
14	4-aminopyridine	9.17	5.13 ± 0.01	N.R.
15	4-(*N*,*N*-dimethylamino)-pyridine	9.71	5.25 ± 0.01	N.R.
16	piperidine	11.1	5.39 ± 0.02	N.R.
17	imidazole	6.65	4.96 ± 0.02	N.R.
18	1-methylimidazole	7.33	5.17 ± 0.02	5.83
19	2-methylimidazole	7.56	5.32 ± 0.02	N.R.
20	1,2-dimethylimidazole	7.85	5.63 ± 0.03	6.63

[a] Schoefield, K. S. "Hetero-Aromatic Nitrogen Compounds"; Plenum Press: New York, 1967; p 146. [b] Reaction: $[(TPP)Ru(CO)] + L \rightleftarrows [(TPP)Ru(CO)(L)]$, in CH_2Cl_2 with 0.1 M TBAP. [c] Reaction: $[(TPP)Ru(CO)]^+ + L \rightleftarrows [(TPP)Ru(CO)(L)]^+$. N.R. = Reaction not observable within the solvent range.

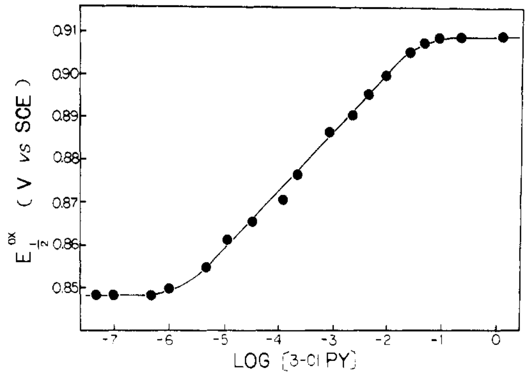

Figure 3. Half-wave potentials for oxidation of (TPP)Ru(CO) in CH_2Cl_2 with 0.1 M TBAP monitored as a function of added 3-chloropyridine. The ionic strength remained constant at 0.1 during the titration.

No change in potential was observed until a concentration consistent with ligand binding was attained. At this point an anodic or cathodic shift of the oxidation potential occurred. For ligands **1–12** the total shift was from 0 to 100 mV in an anodic direction while for ligands **18** and **20** a cathodic shift occurred by 40 and 60 mV, respectively. An example of this shift is shown in Figure 3 for the titration of (TPP)Ru(CO) with 3-chloropyridine. The final invariant potential, obtained at 1 M ligand concentration, is listed in Table III for all of the complexes in which an oxidation is observed.

These electrochemical results for consistent with the spectroscopic results and can be explained on the basis of ligand complexation of $[(TPP)Ru(CO)]^+$ to produce $[(TPP)Ru(CO)(L)]^+$ in solution. At low ligand concentration, (TPP)Ru(CO) is uncomplexed and yields $[(TPP)Ru(CO)]^+$ upon oxidation. However, at higher ligand concentrations (TPP)Ru(CO)(L) was formed in solution and the product of the electrooxidation was $[(TPP)Ru(CO)(L)]^+$, as shown in eq 4.

$$(TPP)Ru(CO)(L) \rightleftarrows [(TPP)Ru(CO)(L)]^+ + e^- \quad (4)$$

Regions of half-wave potential independence at higher ligand concentration confirmed that eq 4 was the prevailing mechanism. Formation constants for ligand addition to the radical

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Table III. Half-Wave Potentials (V vs. SCE) for Oxidation of (TPP)Ru(CO)(L) in CH_2Cl_2 with 0.1 M TBAP Containing 1.0 M Ligand

no.	ligand	pK_{BH^+}[a]	$E_{1/2}$(ox)
	neat CH_2Cl_2		0.85
1	3,5-dichloropyridine	0.67	0.95
2	3-cyanopyridine	1.45	0.93
3	4-cyanopyridine	1.86	0.92
4	3-chloropyridine	2.81	0.91
5	3-bromopyridine	2.84	0.91
6	3-acetylpyridine	3.18	0.90
7	4-acetylpyridine	3.51	0.89
8	pyridine	5.29	0.88
9	3-picoline	5.79	0.87
10	2-picoline	5.96	0.85
11	4-picoline	5.98	0.86
12	3,4-lutidine	6.46	0.85
13	2-aminopyridine	6.82	N.R.[b]
14	4-aminopyridine	9.17	N.R.
15	4-(*N*,*N*-dimethylamino)pyridine	9.71	N.R.
18	1-methylimidazole	7.33	0.81
20	1,2-dimethylimidazole	7.85	0.79

[a] Schoefield, K. S. "Hetero-Aromatic Nitrogen Compounds"; Plenum Press: New York, 1967; p 146. [b] N.R. = Reaction not observable within the solvent range.

(log β_1^+) were calculated under these conditions with eq 3 and are listed in Table II along with values for the neutral complex with the same ligands (log β_1^0). As seen from Table II, values of log β_1^+ are smaller than log β_1^0 for all of the pyridine ligands but the values approach each other with ligands of $pK_a > 5$. Also, with both of the imidazoles for which β_1^0 and β_1^+ could be measured, β_1^+ was greater than β_1^0. These same relative values of log β_1^0 and log β_1^+ for all of the ligands were observed for formation of $[(TPP)Zn(L)]^+$ and [(TPP)Zn(L)], as well as for formation of $[(TPP)Hg(L)]^+$ and (TPP)Hg(L) or $[(TPP)Cd(L)]^+$ and (TPP)Cd(L).[8]

Linear Free Energy Relationships. A large number of linear free energy relationships have been presented in the literature for ligand-addition reactions of metalloporphyrins. Many of these include properties related to the metal–ligand bond strength such as ligand pK_a,[8-17] Gutmann donor number,[18] E_B or C_B values (Drago parameters),[19,20] or some combination of donor parameters.[21] In most cases, for a closely related series of ligands such as the substituted pyridines, linear relationships are obtained. As the ligand set is expanded, however, deviations begin to occur.

One of the most often used correlations with stability constants such as those shown in eq 1 and 2 has been with the ligand pK_a. Although the values utilized are the pK_a values of the conjugate acid in aqueous media, there is a direct physical significance to their use in these correlations. The pK_a's of many nitrogen heterocycles have been shown to correlate with both gas-phase proton affinities[22,23] and lone-pair ionization energies.[24,25] The values of pK_a are also linearly related to the Hammett σ constant. Thus, correlations of stability constants with pK_a allow one to observe deviations of specific ligands in a series (such as sterically hindered ligands) and also allow for a direct comparison of the metal–ligand interaction when the same ligands are added to metalloporphyrins containing different central metals.[8-12] For this reason we have constructed a plot of log β_1^0 and log β_1^+ vs. pK_a. This plot (Figure 4) shows a linear correlation with all of the nonsterically hindered pyridines, as well as with the four imidazoles, two of which may be classified as sterically hindered. The fact that 2-MeIm (ligand **19**) and 1,2-Me_2Im (ligand **20**) fit the relationship indicates that steric hindrance does not play an important role in the stability constants. Similar results on lack of steric hindrance for imidazoles was also observed for ligand additon to $(TPP)M^{II}$ where M = Zn[8] and Mg.[11] This is not true for the sterically hindered pyridines (ligands **10** and **13**), which have greatly reduced values of β_1^0 and β_1^+.

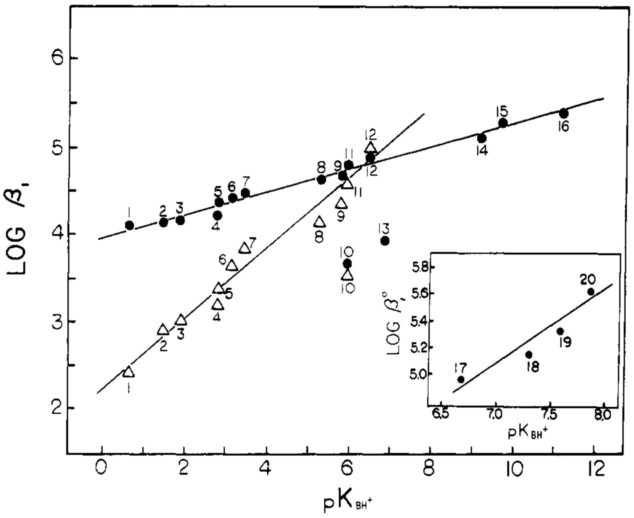

Figure 4. log β_1^0 (●) and log β_1^+ (△) vs. pK_{BH^+} for addition of the substituted pyridines and imidazoles to (TPP)Ru(CO) and $[(TPP)Ru(CO)]^+$. Data for this plot are found in Table II.

A comparison of the slopes of $\Delta \log \beta/\Delta pK_{BH^+}$ has been presented in ref 9. Values of the slopes range from 0.148 for addition of one ligand to ((*p*-OCH_3)TPP)Co to 1.40 for addition of two ligands to $(TPP)FeClO_4$. In this study the slopes $\Delta \log \beta_1^0/\Delta pK_{BH^+}$ and $\Delta \log \beta_1^+/\Delta pK_{BH^+}$ are 0.13 and 0.39 for the non sterically hindered pyridines and 0.52 for correlations with the four imidazole ligands. The fact that all 14 non sterically hindered pyridines fit the correlation of log β_1^0 vs. pK_{BH^+} indicates that σ bonding is dominant in the ligand addition. The increased binding constants of the four imidazole ligands are consistent with some metal π bonding from the Ru(II) to the imidazole in these complexes. At the same time, however, the substantially increased linear slope of $\Delta \log \beta_1^0/\Delta pK_{BH^+} = 0.52$ for the four imidazoles is consistent with the larger σ-donating capability of the imidazoles and suggests that σ bonding predominates in the Ru(II)–ligand bond.

Plots of log β_1^0 and log β_1^+ vs. the substituent constant on the pyridines were also constructed (not shown). The slope of the line for log β_1^0 is 0.83 for the non sterically hindered pyridines with a correlation coefficient 0.95 while that for log β_1^+ is 2.12 with a correlation coefficient of 0.94. The positive ρ values indicate that the σ bonding from ligand to metal influences ligand addition to the ruthenium(II) center. This is consistent with a large number of metalloporphyrin complexes including the five-coordinate complexes (TPP)Zn(L),[8,12,13] (TPP)Mg(L),[11] (TPP)Hg(L),[8b,12] and (TPP)Mn-

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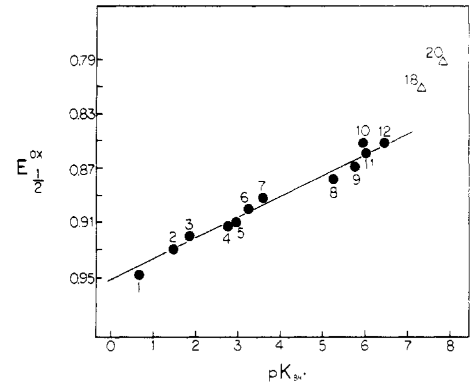

Figure 5. Half-wave potentials vs. ligand pK_{BH^+} for the oxidation of (TPP)Ru(CO)(L) in CH_2Cl_2 with 0.1 M TBAP containing 1 M ligand. The ligand number is referred to in Table III.

(L).[10] However, as in the case of the log $\beta_1{}^0$–pK_{BH^+} plots, a decreased interaction is indicated from the smaller value of ρ. For example, our value of 0.83 may be compared to ρ values of 1.5, 3.1, and 2.2 for the complexes of (TPP)Zn(L), (TPP)Hg(L), and (TPP)Cd(L), respectively.[12] This decrease is undoubtedly due to a strong trans effect of CO, which influences the ligand addition. Trans effects of mixed CO, L complexes are discussed in the literature[26] for (TPP)Ru(CO)(L), (OEP)Os(CO)(L), and (P)Fe(CO)(L) as well as for complexes of (OEP)W(O)(L) and (OEP)Mo(O)(L). For the specific case of the (OEP)Os(CO)(L) complexes (where L was a large variety of ligands), the CO stretching frequencies showed a trans effect that was not explainable by the basicities of the axial ligand trans to CO but rather reflected a balance of σ-donor, π-donor and π-acceptor abilities of the ligands.[26] A similar balancing of effects may be present in the complexes of (TPP)Ru(CO)(L) and would account for the decreased differences in σ-donor effects between the different substituted pyridines.

The same relative change of log $\beta_1{}^0$ and $\beta_1{}^+$ was observed in this study as a function of axial ligand as has been reported for the reactions of (TPP)Zn(L) and $[(TPP)Zn(L)]^+$,[8a] as well as for a similar series involving five-coordinate neutral and oxidized complexes of (TPP)Hg and (TPP)Cd.[8b] In all cases, values of log $\beta_1{}^+$ were initially less than log $\beta_1{}^0$. At the same time, plots of log β_1 vs. pK_a showed greater slopes for cation radical formation such that with ligands of high pK_a a crossover of log $\beta_1{}^+$ and log $\beta_1{}^0$ occurred.

Finally, because the stability constants of the oxidized and reduced forms of the complex are so similar, no substantial shift in redox potential was obtained with the types of ligands investigated in this study. As seen in Table III and in Figure 5 (which plots $E_{1/2}$ vs. pK_a) the maximum change in $E_{1/2}$ from that of the uncomplexed five-coordinate complex (which occurs at 0.85 V) is 100 mV. A total shift of 160 mV was observed between the half-wave potentials of the complex containing 3,5-Cl_2py and that containing 1,2-Me_2Im, but this shift is still far less than for other metalloporphyrins containing bisadducts of the same ligands.

For example, $(TPP)Fe(L)_2 \rightleftarrows (TPP)Fe(L)_2{}^+$ has a maximum shift of 480 mV on going from L = 3,5-dichloropyridine (pK_a = 0.67) to 4-(dimethylamino)pyridine (pK_a = 9.71)[9] while the reaction $(TPP)Os(L)_2 \rightleftarrows (TPP)Os(L)_2{}^+$ has a 240-mV shift in $E_{1/2}$ on changing the ligand from L = pyridine (pK_a = 5.28) to L = piperidine (pK_a = 11.1).[26] Large shifts in $E_{1/2}$ are also observed for $(TPP)M^{II} \rightleftarrows (TPP)M^{III}$ reactions when the central metal is Co[27] or Cr,[28] and identical ligands such as those in Table I are bound to the central metal.

On the other hand, when one of the axial ligands is CO and the other is a nitrogenous base such as in the case of (OEP)Os(CO)(L), very little change is observed in the M(II) $\rightleftarrows$ M(III) reaction. For example, only a 60-mV shift in the Os(II) $\rightleftarrows$ Os(III) reaction is observed between the complexes where one of the ligands is CO and the other is 1-MeIm or piperidine.[26] This compares to an 80-mV difference for the same two sets of ligands with (TPP)Ru(CO)(L).

In summary, only small changes in $E_{1/2}$ are observed for the oxidation of (TPP)Ru(CO)(L), where L is a σ-donor ligand of the type utilized in this study. This is true despite the fact that large values of stability constants are obtained for formation of (TPP)Ru(CO)(L) from (TPP)Ru(CO) and is due to a compensating effect of similar stability constants for formation of $[(TPP)Ru(CO)(L)]^+$ from $[(TPP)Ru(CO)]^+$. This similarity is perhaps not unexpected since oxidation at the π ring system affects the central metal only to the extent of changing the electron density at the central metal by inductive effects. This would suggest that in order to substantially modify redox potentials of ruthenium(II) porphyrins, more substantial changes in the nature of the trans ligand or in the porphyrin plane are needed. These studies are presently under way using both novel substituted metalloporphyrin structures and π-acceptor ligands.

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Registry No. (TPP)Ru(CO)(3,5-dichloropyridine), 82555-27-9; (TPP)Ru(CO)(3-cyanopyridine), 82555-28-0; (TPP)Ru(CO)(4-cyanopyridine), 82555-29-1; (TPP)Ru(CO)(3-chloropyridine), 82555-30-4; (TPP)Ru(CO)(3-bromopyridine), 82555-31-5; (TPP)Ru(CO)(3-acetylpyridine), 82555-32-6; (TPP)Ru(CO)(4-acetylpyridine), 82555-33-7; (TPP)Ru(CO)(pyridine), 41751-82-0; (TPP)Ru(CO)(3-picoline), 82555-34-8; (TPP)Ru(CO)(2-picoline), 82555-35-9; (TPP)Ru(CO)(4-picoline), 82555-36-0; (TPP)Ru(CO)(3,4-lutidine), 82555-37-1; (TPP)Ru(CO)(2-aminopyridine), 82555-38-2; (TPP)Ru(CO)(4-aminopyridine), 82555-39-3; (TPP)Ru(CO)(4-(*N*,*N*-dimethylamino)pyridine), 82555-40-6; (TPP)Ru(CO)(piperidine), 60507-99-5; (TPP)Ru(CO)(imidazole), 32242-24-3; (TPP)Ru(CO)(1-methylimidazole), 82555-41-7; (TPP)Ru(CO)(2-methylimidazole), 82555-42-8; (TPP)Ru(CO)(1,2-dimethylimidazole), 82555-43-9.

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