Spectroscopic and Oxidation Studies of *meso*-Tetraphenyltetrabenzoporphyrin Carbonyl Complexes of Ruthenium(II): CO as the Probe to Elucidate the Bonding Characteristics of Porphyrins

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The carbonyl complex of (*meso*-tetraphenyltetrabenzoporphyrinato)ruthenium(II), Ru(TPTBP)(CO), has been synthesized and characterized by FABMS, UV/vis, ^{1}H NMR, and IR spectroscopy. Six-coordinate complexes Ru(TPTBP)(CO)(L) with different π-bonding-capability ligands (L = NEt_3, pip, 1-MeIm, py, PBu_3) coordinated trans to CO have been studied. The shifts in ν_{CO} for this series of complexes are consistent with the existence of M → CO π-back-bonding. In contrast to what would be expected by nitrogen basicity, ν_{CO} values for Ru(TPTBP)(CO), Ru(TPP)(CO), and Ru(OEP)(CO) are 1959, 1930, and 1917 cm^{-1}, respectively. This result suggests that TPTBP should be both a better σ-donor and a better π-acceptor than normal porphyrin systems (P). Oxidation studies of Ru(TPTBP)(CO), Ru(TPTBP)(CO)(py), and Ru(TPTBP)$(py)_2$ have been carried out both electrochemically and chemically. ^{1}H NMR, ESR, and electronic spectroscopic studies suggest that there are two different types of oxidation products. The sites of oxidation should both be on the porphyrin ring to give two different types of ruthenium(II) porphyrin π-cation radicals $[Ru^{II}(TPTBP)^{\bullet+}(L)(L')]X$ of A_{1u} and A_{2u} character, respectively. In marked contrast to other ruthenium porphyrins reported in the literature, extraplanar ligands in the Ru(TPTBP) system do not affect the site of oxidation (metal vs ring) but only mediate the level of oxidation on the ring (a_{1u} vs a_{2u}). These results can be ascribed to the extended π-system and the ring deformation of the TPTBP porphyrin macrocycle and are also consistent with the fact that TPTBP is a stronger π-acceptor than other porphyrin systems.

Introduction

Metalloporphyrins serve many diverse functions in biological systems. They may change from an oxygen carrier to an oxygen activation catalyst just by protein fine-tuning of the strucuture around the coordination sphere. The chemical variation of biologically active molecules represents a very successful method for the elucidation of structure−property−activity interrelationships. A knowledge of these interrelationships may help to sort out the essential electronic parameters that govern the specific action of the heme proteins in biologic oxygen transport and redox processes. Other than the electronic and steric effects that can be introduced through different substituents on the porphyrin macrocycle, the functional consequences of nonplanar distortions are of current interest. Fajer suggested that conformational variations provide an attractively simple mechanism for varying a wide range of chemical and physical properties of porphyrinic chromophores and prosthetic groups *in vitro* and *in vivo*.[1] These deformations result from intramolecular steric interactions among the peripheral substituents *in vitro*, which are believed to be introduced by the combinations of hydrogen bonding, axial ligation, and nearby protein residues *in vivo*.

Tetraphenyltetrabenzoporphyrin (TPTBP) is a structural hybrid of tetraphenylporphyrin (TPP) and tetrabenzoporphyrin (TBP). Our previous work showed that, other than the extended π-electron system, macrocycle of TPTBP is severely distorted into a saddle shape both in the solid state[2] and in solution.[3] The consequences of saddle deformation on the properties of the nonplanar tetrabenzoporphyrin are significant. As reported previously, the cumulative effects of conformational changes and substituent addition are reflected in the red-shifted optical spectrum, diminished fluorescence,[4] increased basicity (pK_3 = 5.75 for $TPTBPH_2$ versus 3.95 for $TPPH_2$), and ease of oxidation of the neutral compound ($E_{1/2}$ = +0.42 V for Zn(TPTBP) versus +0.75 V for Zn(TPP)). These features should result in different bonding characteristics in the corresponding metalloporphyrin complexes. Cis, trans, and metal effects mediated by the bonding properties of porphyrins have been reviewed extensively by Buchler et al.[5]

As a typical π-acid and the widely opened IR region for ν_{CO} stretching frequencies, CO is a good probe to elucidate the bonding properties of porphyrins. Carbonyl complexes of iron porphyrins are stable only in the

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presence of excess CO or in the solid state. The group homologue of iron, ruthenium, is expected to show a much stronger metal-to-ligand π-back-bonding in its +II oxidation state and form more stable complexes with CO than with iron. Both cis and trans effects should be exaggerated with ruthenium porphyrins. On the other hand, resonance Raman studies showed that π-back-bonding to the porphyrin appears to be quantitatively similar for Ru(II) and Fe(II).[6] Therefore, Ru(TPTBP)(CO) will be the first candidate for these series of systematic studies.

Experimental Section

Physical Measurements. ^{1}H NMR spectra were recorded on a Varian Gemini-200 or VXR-300 spectrometer. Electronic spectra were measured with a Hitachi U-3210 spectrophotometer. Infrared spectra were recorded on a Hitachi IR-270 spectrophotometer as a KBr disk or in CH_2Cl_2 solution. ESR spectra were recorded at the X band with a Bruker spectrometer. Mass spectra were obtained using a JEOL JMS-HX110 high-resolution double-focusing mass spectrometer equipped for fast atom bombardment analysis.

Cyclic voltammetry was performed in CH_2Cl_2 solution that was 0.10 M in supporting electrolyte and 1.5−3.5 mM in metalloporphyrin. The supporting electrolyte was tetra-*n*-butylammonium perchlorate. A conventional three-electrode system was used. Two Pt buttons served as the working electrode and the counter electrode. All potentials in this paper are reported *vs* the SCE. Measurements were made with a Bioanalytical Systems Model BAS CV-27 potentiostat.

Chemical oxidations of ruthenium porphyrin complexes in dilute CH_2Cl_2 solutions were carried out by a spectrophotometric titration procedure using I_2 or Br_2 solutions. A stoichiometric amount of oxidant is enough for complete oxidation.

The preparation of Zn(TPTBP) was a modification of the procedures published previously by Kopranekov et al.[7] and Ichimura et al.[8]

(Tetraphenyltetrabenzoporphyrinato)zinc, Zn(TPTBP). A homogeneous mixture of phthalimide (0.735 g, 5 mmol), phenylacetic acid (1.5 g, 10 mmol), and zinc benzoate (1.51 g, 5 mmol) was put into a 25 mL round-bottom flask and heated at 360 °C for 40 min under an N_2 atmosphere. After the mixture was cooled, the dark green solid was reduced to a powder, washed several times with hot water and hexane, and finally dissolved in CH_2Cl_2 and the solution filtered. This procedure also yields a substantial amount of the triphenyl derivative. Purification was accomplished by repeated chromatography of the filtrate with different ratios of hexane/CH_2Cl_2, first on a column of aluminum oxide (Merck 1097) and then on a column of silica gel. The product was finally recrystallized from CH_2Cl_2/hexane, and the average yield was around 10%. MS: $(M)^+$ *m/e* 876.

Tetraphenyltetrabenzoporphyrin, TPTBPH$_2$. Zn(TPTBP) (100 mg) was dissolved in about 50 mL of CH_2Cl_2, treated with 100 mL of 15% HCl aqueous solution, and then neutralized with sodium acetate. Further purification was carried out by chromatography on a column of silica gel with hexane/CH_2Cl_2 and recrystallization from CH_2Cl_2/hexane. MS: $(M + H)^+$ *m/e* 815.

Carbonyl(tetraphenyltetrabenzoporphyrinato)ruthenium(II), Ru(TPTBP)(CO). The preparation and characterization of ruthenium(II) carbonyl porphyrin complexes have been described in the literature. The method we used for insertion of ruthenium into TPTBP is a modification of the procedure of Rillema *et al.* for the synthesis of Ru(TPP)(CO).[9] In a typical experiment, 100 mg of $TPTBPH_2$ and 100 mg of $Ru_3(CO)_{12}$ in 30 mL of decalin was refluxed under nitrogen for about 4 h. After it was cooled to room temperature, the reaction mixture was loaded on a column of silica gel and eluted with varying ratios of hexane/CH_2Cl_2/acetone. Recrystallization from CH_2Cl_2/hexane gave pure Ru(TPTBP)(CO) with an average yield of 57%. MS: $(M)^+$ *m/e* 942, $(M - CO)^+$ *m/e* 914. HRMS calcd for $C_{61}H_{36}ON_4Ru$: $(M)^+$ *m/e* 942.1933; found *m/e* 942.1937 ($\Delta = 0.4$).

Bis(pyridine)(tetraphenyltetrabenzoporphyrinato)ruthenium(II), Ru(TPTBP)(py)$_2$. Following earlier workers[10] a solution of 100 mg of Ru(TPTBP)(CO) in 70 mL of pyridine was irradiated with a 450 W mercury lamp (Pyrex filter) for 12 h, while the solution was continually flushed with nitrogen. The solution was then reduced to dryness, followed by column chromatography and recrystallization from CH_2Cl_2/hexane. An average yield of 68% was obtained. MS: $(M)^+$ *m/e* 1072, $(M - 2py)^+$ *m/e* 914. HRMS calcd for $C_{70}H_{46}N_6Ru$: $(M)^+$ *m/e* 1072.2827; found *m/e* 1072.2833 ($\Delta = +0.5$ ppm).

Carbonyl(pyridine)(tetraphenyltetrabenzoporphyrinato)ruthenium(II), Ru(TPTBP)(CO)(py). In a typical experiment, 100 mg of Ru(TPTBP)(CO) in 30 mL of CH_2Cl_2 was treated with 9 μL of pyridine at room temperature. The solution was then reduced to dryness, followed by recrystallization from CH_2Cl_2/hexane to give Ru(TPTBP)(CO)(py) in quantitative yield. The complete conversion of Ru(TPTBP)(CO) into Ru(TPTBP)(CO)(py) was checked by TLC and confirmed by ^{1}H NMR, UV/vis, and IR spectra (Figure 1b and Table 1). MS: $(M)^+$ *m/e* 1021, $(M - py)^+$ *m/e* 942, $(M - py - CO)^+$ *m/e* 914. HRMS: calcd for $C_{66}H_{41}ON_5Ru$ $(M)^+$ *m/e* 1021.2355; found *m/e* 1021.2364 ($\Delta = +0.9$ ppm).

Carbonyl(1-methylimidazole)(tetraphenyltetrabenzoporphyrinato)ruthenium(II), Ru(TPTBP)(CO)(MeIm). This complex and all the following series of complexes were generated *in situ* for spectroscopic studies. Typically, a 0.5% CH_2Cl_2 solution of 1-methylimidazole (68 μL, 0.0041 mmol) was added in small portions to a solution of Ru(TPTBP)(CO) (3.5 mg, 0.0037 mmol) in CH_2Cl_2 (17.5 mL). The conversion of Ru(TPTBP)(CO) into Ru(TPTBP)(CO)(MeIm) was monitored by UV/vis and IR spectra. Similar titration was carried out in $CDCl_3$ for ^{1}H NMR studies. Spectroscopic data are collected in Table 1.

Carbonyl(piperidine)(tetraphenyltetrabenzoporphyrinato)ruthenium(II), Ru(TPTBP)(CO)(pip). This complex was prepared with piperidine as above. Spectroscopic data are collected in Table 1.

Carbonyl(triethylamine)(tetraphenyltetrabenzoporphyrinato)ruthenium(II), Ru(TPTBP)(CO)(NEt$_3$). This complex was prepared in a similar manner, except that addition of excess triethylamine (~20 equiv) is necessary for the formation of Ru(TPTBP)(CO)(NEt_3). The conversion of Ru(TPTBP)(CO) into Ru(TPTBP)(CO)(NEt_3) was monitored by UV/vis and IR spectra. Similar titration was carried out in $CDCl_3$ for ^{1}H NMR studies. Spectroscopic data are collected in Table 1.

Carbonyl(tri-*n*-butylphosphine)(tetraphenyltetrabenzoporphyrinato)ruthenium(II), Ru(TPTBP)(CO)(PBu$_3$), and Bis(tri-*n*-butylphosphine)(tetraphenyltetrabenzoporphyrinato)ruthenium(II), Ru(TPTBP)(PBu$_3$)$_2$. A 2% CH_2Cl_2 solution of tri-*n*-butylphosphine (43 μL, 0.0042 mmol) was added in ~10 μL portions to a solution of Ru(TPTBP)(CO) (4 mg, 0.0042 mmol) in CH_2Cl_2 (20 mL). The conversion of Ru(TPTBP)(CO) into Ru(TPTBP)(CO)(PBu_3) was monitored by UV/vis and IR spectra. Similar titration was carried out in $CDCl_3$ for ^{1}H NMR studies. Addition of more than 1 equiv of tri-*n*-butylphosphine induces decarbonylation and formation of Ru(TPTBP)(PBu_3)$_2$. Ru(TPTBP)(PBu_3)$_2$ was

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Table 1. Electronic, ^{1}H NMR, and IR Spectral Data for Ru(TPTBP) Complexes

complex	UV/vis		^{1}H NMR α	β	*o*	*m, p*	ν_{CO}
Zn(TPTBP)	460	607, 651	7.16	7.26	8.28	7.89	
Ru(TPTBP)(CO)	418, 446	576, 622	7.05	7.2	8.3	7.9	1959
Ru(TPTBP)(CO)(py)	422, 448	578, 620	7.0	7.2	8.22, 8.34	7.89	1968
Ru(TPTBP)(CO)(MeIm)	424, 446	578, 620	7.0	7.2	8.22, 8.34	7.89	1965
Ru(TPTBP)(CO)(pip)	426,446	574, 618	7.05	7.25	8.25, 8.35	7.9	1956
Ru(TPTBP)(CO)(NEt_3)	428, 448	578, 622	7.04	7.2	8.25, 8.35	7.9	1930
Ru(TPTBP)(CO)(PBu_3)	438, 458	584, 624	6.95	7.1	8.2, 8.28	7.85	1978
Ru(TPTBP)$(py)_2$	372, 410, 436	544, 616	6.8	7.0	8.24	7.82	
Ru(TPTBP)$(PBu_3)_2$	332, 458	556, 624	6.8	7.0	8.2	7.82	

generated quantitatively with 2 equiv of PBu_3 (86 μL, 0.0085 mmol). Spectroscopic data are summarized in Table 1.

Results and Discussion

Spectroscopic Characterizations of Ruthenium(II) Tetraphenyltetrabenzoporphyrins. The preparation and characterization of RuP(CO)L, RuP$(py)_2$, and RuP$(PBu_3)_2$ complexes for tetraphenylporphyrin (TPP) and octaethylporphyrin (OEP) systems have been described.[11] These procedures work similarly for tetraphenyltetrabenzoporphyrin (TPTBP).

FAB/MS is suitable for the confirmation of ruthenium insertion. Other than CO, most axial ligands trans to CO are too weak to remain coordinated during ionization. However, most axial ligands are easily identified in ^{1}H NMR spectra. All resonances corresponding to axial ligands are upfield-shifted through the anisotropic ring current effect of the porphyrin macrocycle. Typical ^{1}H NMR spectra are shown in Figure 1 for Ru(TPTBP)(CO), Ru(TPTBP)(CO)(py), and Ru(TPTBP)$(py)_2$.

As can be seen in Figure 1b,c, the intensities of the upfield-shifted resonances clearly indicate the number of coordinated pyridine groups in the complexes to be one and two, respectively. The split ortho resonances in Figure 1a,b further confirm different coordination environments on two sides of the porphyrin plane. With the coordination of the second pyridine in the bis(pyridine) complex, α-py shifts downfield while *β*-py and *γ*-py shift upfield. This pattern suggests a stronger and shorter Ru−py bond in the bis(pyridine) complex than in the carbonyl pyridine complex. This is consistent with the fact that strong trans influence from CO will make the trans pyridine weak. On the other hand, without the coordination of CO, all peaks from α,*β*-protons of the porphyrin macrocycle shift upfield for Ru(TPTBP)$(py)_2$. The increased charge density on the porphyrin ring has been suggested as a result of enhanced metal to porphyrin *π*-back-bonding.[5]

NMR data for the series of ruthenium(II) complexes we studied are summarized in Table 1. No peaks corresponding to the coordinated ligand were detected with the addition of 1 equiv of NEt_3 to the Ru(TPTBP)(CO) solution. Therefore, Ru(TPTBP)(CO)(NEt_3) was generated in solution in the presence of excess ligand to avoid ligand dissociation in dilute solution. Coordination of NEt_3 is visible from minor changes of the ring

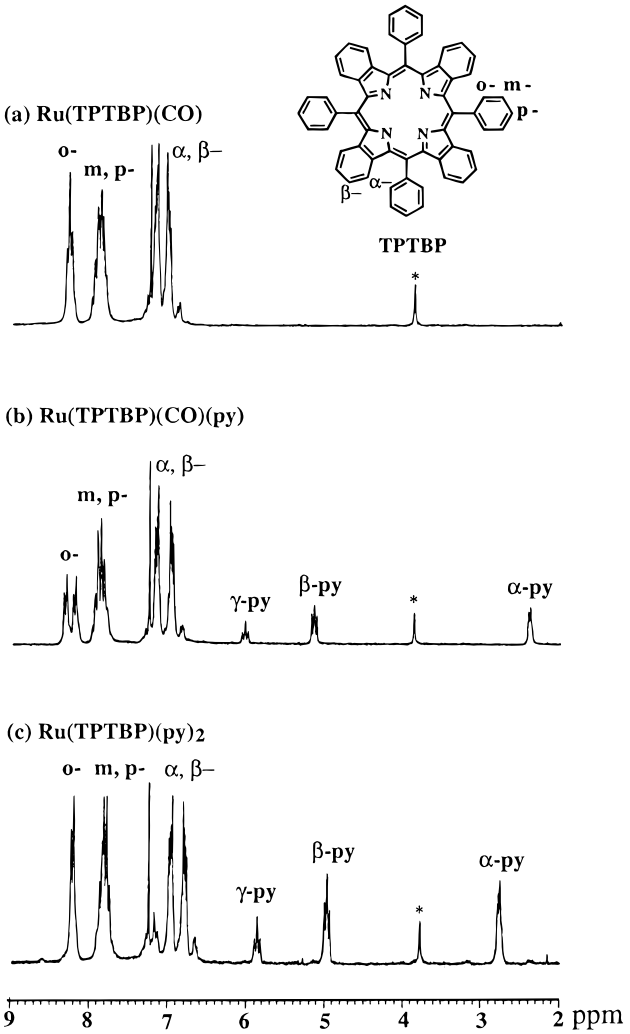

Figure 1. 200 MHz ^{1}H NMR spectra of (a) Ru(TPTBP)(CO), (b) Ru(TPTBP)(CO)(py), and (c) Ru(TPTBP)$(py)_2$ taken in $CDCl_3$ at room temperature.

resonances and the corresponding UV/vis and IR spectral changes (*vide infra*).

Typical electronic absorption spectra are shown in Figure 2 for Zn(TPTBP), Ru(TPTBP)$(py)_2$, Ru(TPTBP)(CO), and Ru(TPTBP)(CO)(py). Table 1 also includes peak optical absorption data for all the ruthenium(II) complexes we studied. In comparison with the normal type spectrum of Zn(TPTBP), the Q bands of carbonyl complexes of ruthenium(II) are very prominent as well as substantially blue-shifted (ca. 30 nm). The ratio $\epsilon_{max}(B)/\epsilon_{max}(Q)$ is anomalously low compared to that for normal metalloporphyrins. There is a pronounced shoulder to the blue side of the Soret band; otherwise, the spectrum would seem to be typically hypso.[10] The electronic absorption data of these Ru(II) carbonyl

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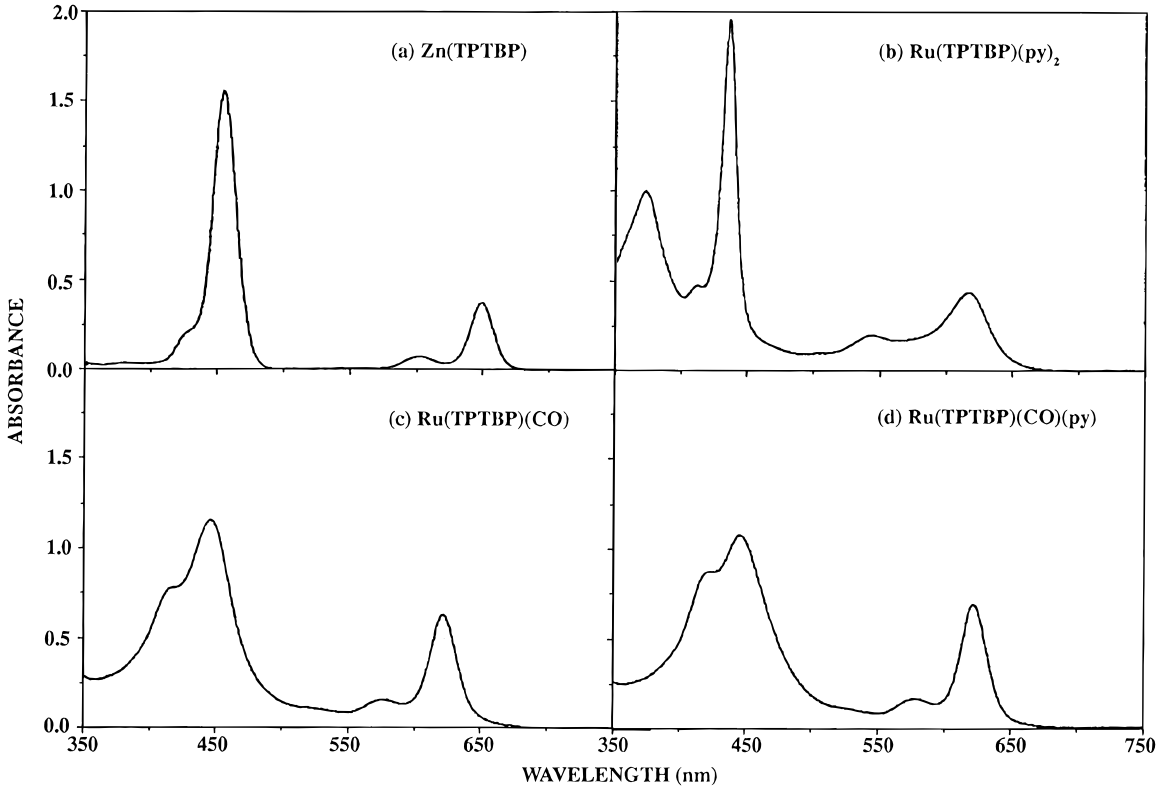

Figure 2. UV/vis spectra of (a) Zn(TPTBP), (b) Ru(TPTBP)$(py)_2$, (c) Ru(TPTBP)(CO), and (d) Ru(TPTBP)(CO)(py) taken in CH_2Cl_2.

porphyrin complexes can be interpreted in terms of a Gouterman four-orbital model modified by the inclusion of the metal dπ orbitals. Increased metal-to-porphyrin π-back-bonding promotes mixing of $e_g(\pi^*)$ and $e_g(d\pi)$ orbitals, with the result that the $\pi \rightarrow \pi^*$ transitions fall at higher energies than those of a metal complex without this π-bond interaction. The magnitude of the hypsochromic shifts has been correlated with the π-donor ability of the metal ion or the π-acceptor ability of the porphyrin ring.[10] The amount of the shifts for the TPTBP system is about twice the similar shifts for the TPP system (i.e. 30 nm vs 16 nm). This may suggest that TPTBP is a stronger π-acceptor than TPP.

In Figure 2b, the bis(pyridine) complex, which shows other intense absorption besides normal bands, gives a very clear example of the hypso/hyper type spectrum. Dramatic differences were found in comparing the visible spectrum of Ru(TPTBP)$(py)_2$ with that of Ru(TPP)$(py)_2$,[11d] consistent with different π-bonding capabilities between TPTBP and TPP.

ν_{CO} data for Ru(TPTBP)(CO)(L) complexes are sensitive to the bonding ability of trans ligands L. L ligands with stronger π-acidity will compete for the π-electron density from the central metal, thus reducing M→CO π-back-bonding. On the basis of the available ν_{CO} data for these series of Ru(TPTBP)(CO)(L) complexes, as shown in Table 1, the following sequence of π-acidity of trans ligands can be obtained: PBu_3 > py > 1-MeIm > pip > NEt_3.

Comparison of ν_{CO} data between different porphyrin systems can be informative (Table 2). The higher π-acidity of TPTBP compared to other porphyrin-related macrocycles is apparent in the CO stretching frequencies of metal carbonyl complexes of these macrocycles. Greater metal-to-macrocycle back-bonding in Ru(TPTBP)(CO) reduces the metal-to-CO back-bonding, as evidenced by higher CO stretching frequencies. Actually, part of the effect due to increased π-acidity is compensated by the increased σ-basicity. Larger porphyrin-to-metal σ-donation should increase the metal-to-CO back-bonding. The difference in ν_{CO} between Ru(TPP)(CO) and Ru(OEP)(CO) is mainly induced by different σ-basicities, as evidenced by the values of pK_3. Therefore, TPTBP is apparently a stronger σ-donor and π-acceptor than other porphyrin-related macrocycles.

Table 2. Comparison of ν_{CO} Values for RuP(CO) Complexes with Basicities of Porphyrin Free Base

complex	Ru(TPTBP)(CO)	Ru(TPP)(CO)	Ru(OEP)(CO)
$\nu_{CO}(cm^{-1})$	1959	1930[a]	1917[a]
pK_3	5.75	3.95	4.36

[a] Reference 11d.

Oxidation Studies of Ru(TPTBP)(CO), Ru(TPTBP)(CO)(py), and Ru(TPTBP)$(py)_2$. Cyclic voltammograms were measured for Ru(TPTBP)(CO), Ru(TPTBP)(CO)(py), and Ru(TPTBP)$(py)_2$ complexes in CH_2Cl_2 solution with TBAP as the electrolyte. The bis(pyridine) species show three reversible one-electron oxidations, while the other two species reveal only two reversible one-electron oxidations within the solvent limits (Table 3). The first one-electron-oxidation process could be accomplished chemically by the addition of Br_2 or I_2 in CH_2Cl_2 solution. Visible spectra of the one-electron-oxidation products of Ru(TPTBP)(CO) and Ru(TPTBP)$(py)_2$ are shown in Figure 3. Oxidation products of both Ru(TPTBP)(CO) and Ru(TPTBP)(CO)(py) gave very similar spectral changes. All the visible spectral changes reveal several isosbestic points with less intense absorptions, similar to those of other well-characterized porphyrin π-cation radicals. These porphyrin π-cations exhibited a typical ESR signal for a

Table 3. Electrochemical and EPR Values for Ruthenium Porphyrin Complexes

	$E_{1/2}$				
	O_1				
complex	PRu^{II}/PRu^{III}	$PRu^{II}/P^{\bullet+}Ru^{II}$	O_2	O_3	g(77 K) after first oxidn
Ru(TPTBP)(CO)		0.49	0.93		2.000[a]
Ru(TPTBP)(CO)(py)		0.56	1.10		1.999[a]
Ru(TPTBP)$(py)_2$		0.36	0.94	1.38	2.000[b]
Ru(TPP)(CO)[c]		0.82	1.21		2.004
Ru(TPP)(CO)(py)[c]		0.81	1.36		2.007
Ru(TPP)$(py)_2$[c]	0.21		1.26		
Ru(OEP)(CO)[c]		0.64	1.21		2.004
Ru(OEP)$(py)_2$[c]	0.08				

[a] ESR active at room temperature. [b] ESR silent at room temperature. [c] Reference 11d.

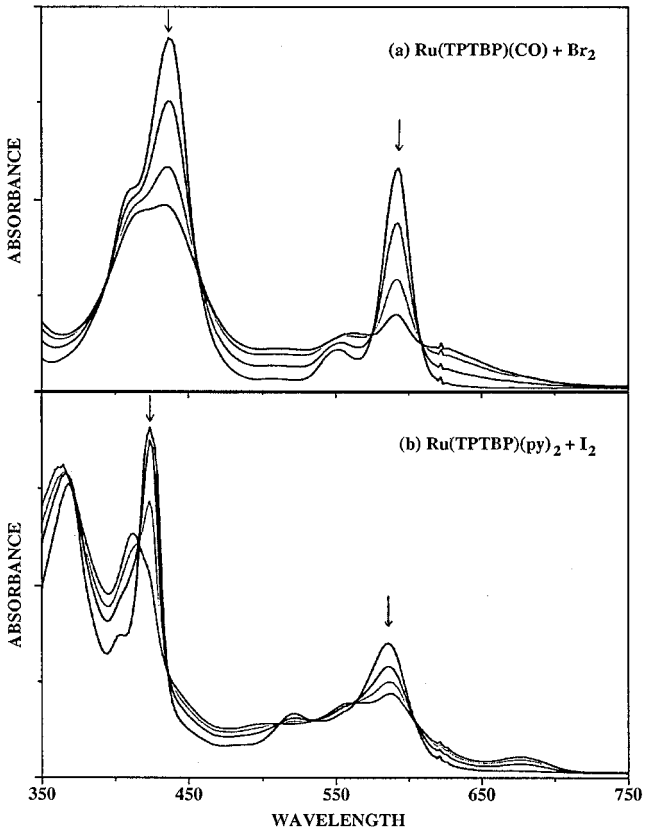

Figure 3. Visible spectral changes during the one-electron oxidation of (a) Ru(TPTBP)(CO) with Br_2 and (b) Ru(TPTBP)$(py)_2$ with I_2 in CH_2Cl_2.

free radical at 77 K. Although radicals of the carbonyl complexes gave single-line ESR signals with $g \approx 2.0$ at room temperature, the radical of the bis(pyridine) complex showed a less intense signal with $g \approx 2.0$ only at 77 K.

Consistent with the ESR results, while the ^{1}H NMR spectrum of the oxidation product of the bis(pyridine) complex was well-resolved (Figure 4b), parts of the spectra of the corresponding carbonyl complexes were beyond detection due to too much broadening (Figure 4a). Similar ^{1}H NMR and ESR spectral features have been reported for $[Ru^{II}(OEP)^{\bullet+}(CO)]Br$ and $[Ru^{II}(OEP)^{\bullet+}(CO)]ClO_4$ π-cation radicals which possess predominant A_{2u} and A_{1u} character, respectively.[12] All these results suggest that both CO and bis(pyridine)

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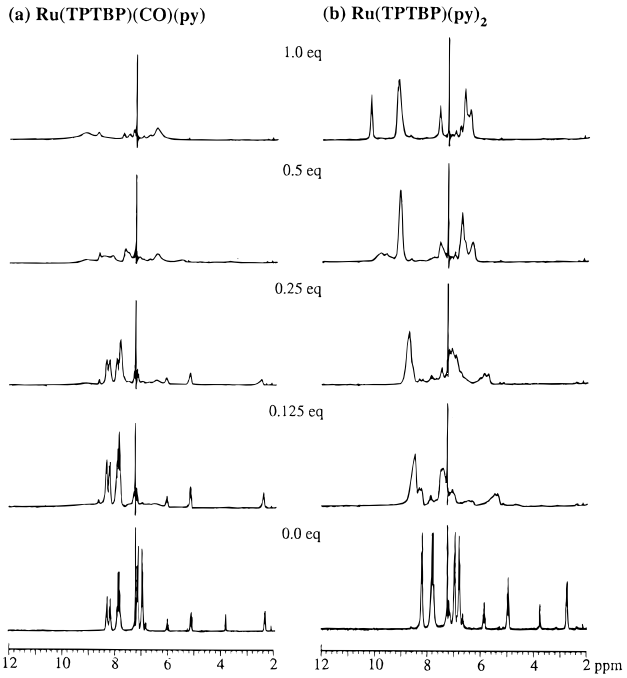

Figure 4. 200 MHz ^{1}H NMR spectral changes during the one-electron oxidation of (a) Ru(TPTBP)(CO)(py) and (b) Ru(TPTBP)$(py)_2$ with Br_2 in $CDCl_3$.

complexes were ring-oxidized to form two different types of porphyrin π-cation radicals. The carbonyl complexes are predominantly of A_{1u} character, and the bis(pyridine) complex is mainly of A_{2u} character.

It is well-documented that the CO complex of ruthenium(II) porphyrin electrochemically or chemically undergoes ring oxidation to form the π-cation radical $[Ru^{II}P^{\bullet+}(CO)L]^+$. However, in normal porphyrin systems, one-electron oxidation of carbonyl-free $Ru^{II}P(py)_2$ species occurs at the metal to give $[Ru^{III}P(py)_2]^+$.[11d] The presence of CO in ruthenium porphyrins causes large anodic shifts for the first oxidation (~0.6 V from Table 3), making the CO complexes much more difficult to oxidize and resulting in a change in oxidation site. For the TPTBP system, the corresponding anodic shift is no larger than 0.2 V and is more consistent with oxidation at the same site, namely, the TPTBP ligand.

Due to the extended π-system and the ring deformation of the TPTBP porphyrin macrocycle, it is reasonable that energy levels of the highest occupied π molecular orbitals (a_{1u} and a_{2u}) are higher than that of the metal dπ orbitals in both CO and bis(pyridine) complexes. Differences in π-back-bonding ability between CO and pyridine are not sufficient to invert the relative energy of metal dπ and TPTBP π MO levels; they only exchange the order of a_{1u} and a_{2u} π MO's. Previous ENDOR studies showed that Zn(TPTBP) was oxidized to give an A_{2u} π-cation radical and suggested that in the TPTBP system a_{2u} should be higher than a_{1u} in energy.[1c] However, with the strong π-acid CO coordinated at the axial position, porphyrin will engage more as a π-donor; the a_{2u} π MO which is mainly responsible for the P→M π donation might be depressed in energy and result in an a_{1u} π-cation radical upon oxidation.

In contrast to other ruthenium porphyrins reported in the literature, extraplanar ligands in the Ru(TPTBP) system do not affect the site of oxidation (metal vs ring) but only mediate the level of oxidation on the ring (a_{1u}

vs a_{2u}). This rationalization is also consistent with the above data that TPTBP, in comparison to normal porphyrins, is an exceptionally good π-acceptor in the absence of CO. At this stage, it is hard to rationalize whether the saddle-shaped deformation or extended π-system of TPTBP is mainly responsible for its π-acidity. The consequences of these special bonding characteristics of TPTBP on the coordination chemistry of other transition-metal complexes are currently underway in our laboratory.

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