

ried out under an inert atmosphere using Schlenk techniques, VAC HE-493 dry box and vacuum line techniques. The solvent were freshly distilled prior to use. Deuterated solvents were degassed *via* the freeze-thaw method. Tungsten(VI) hexachloride, Triphenylphosphine and Sodiumborotetrahydride were used as purchased from Aldrich Chemical Co. The complex, $WCl_4(PPh_3)_2$ were prepared by the literature method.¹⁵ Infrared spectra were recorded on a Midac Model M-1200 spectrometer from 600 to 4000 cm^{-1} as pressed KBr pellets. 1H NMR and ^{31}P NMR spectra were collected on Bruker AM 500 MHz NMR spectrometer in 5 mm tubes. Residual Proton in deuterated solvents were used as internal standards for the 1H NMR spectrum. Phosphorus chemical shifts was referenced to external 85% H_3PO_4 . T_1 measurements were performed on Bruker AM 300 MHz NMR at KBSC Seoul branch.

Preparation of $WH_4(PPh_3)_3$. A suspension of $WCl_4(PPh_3)_2$ (6.00 g, 6.60 mmol) and $NaBH_4$ (3.00 g, 78.0 mmol) in the presence of excess PPh_3 (3.36 g, 12.0 mmol) were vigorously stirred in EtOH (60 mL) at room temperature for 6 h. The mixture was filtered through glass filter and washed with EtOH (60 mL) and dried in vacuo. Then the solid was dissolved in diethylether (250 mL) and filtered through glass filter. The remaining solid was dissolved in benzene (250 mL) again and filtered. Then, the filtrate was concentrated (50 mL) *in vacuo* and slowly evaporated to obtain off-white crystals (2.72 g, 43.4%). 1H NMR (C_6D_6) δ -0.33 (q, $J_{P-H}=36$ Hz, $J_{W-H}=26.6$ Hz), 6.91 (m, Ph), 7.71 (m, Ph); ^{31}P NMR (C_6D_6) δ 42.11. I.R. (KBr) 3049 (m), 1954 (m), 1769 (s), 1431 (s), 1088 (s), 694 (s), 520 (s) cm^{-1} . Anal. Calcd for $C_{54}H_{51}P_3W$: C, 66.4; H, 5.30. Found: C, 66.0; H, 5.80.

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Spectroscopic Study of a Series of Para-Substituted Tetraphenylporphine Carbonyl Complexes of Ruthenium(II) Containing Nitrogenous Bases

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The study of carbonyl complexes of ruthenium porphyrins has been intensively investigated by comparing with those of the corresponding iron hemes,¹⁻⁴ since the Ru metal ion has been established to serve as a suitable substitute for the Fe metal ion. More interestingly, six-coordinate ruthenium(II) carbonyl-porphine complexes containing nitrogenous base had a tendency to undergo inter- and intramolecular site exchange reactions, which were well investigated by total line shape analysis of the variable temperature nmr spectra.⁵⁻⁷ The unusual lability of these ruthenium complexes has considerable interests in their structures and properties. The structural effects on the molecular properties of the planar and nonplanar metalloporphyrin complexes were studied using spectroscopic,⁸ photodynamic,⁹ and electrochemical methods.¹⁰

It is generally supported the formulation of $Ru(TPP)(CO)$ by the reaction of Ru_3CO_{12} with TPP (TPP = *meso*-tetraphenylporphine), which considered to be five-coordinate Ru(II) complex.¹ The complexation of $Ru(TPP)(CO)$ with nitrogenous bases was assumed to involve coordination in the vacant sixth axial position. Six-coordinate ruthenium complexes with other bases have been known.^{5,11} Previously the crystal structures of $Ru(TPP)(CO)(Base)(Base = \text{pyridine, ethanol, and 1-Melm})$ were reported.¹²⁻¹⁴

The present work is concerned with the synthesis of six-coordinate *para*-substituted tetraphenylporphine ruthenium(II) carbonyl complexes, $Ru(p\text{-XTPP})(CO)(\text{Nitrogenous Base})$ (X = MeO, NO₂, F, and Cl, Nitrogenous Base = Py, Im, 1-Melm, and 1,2-Me₂Im)¹⁵ to investigate the electronic effect of the sixth ligand and/or porphine derivatives on ruthenium carbonyl bond.

Experimental Section

Solvents used in the metalloporphyrins' syntheses were distilled and purified. Reagent grade *p*-chlorobenzaldehyde and *p*-nitrobenzaldehyde were purified by recrystallization from ethanol and water. Metalloporphyrins were prepared

by a literature method.¹⁵ All other reagents were purchased commercially as reagent grade chemicals and used without further purification.

Melting points were determined with a Melt-Temp block and were uncorrected. Infrared measurements were obtained as KBr pellets by using either a Nicolet 5MX-S or MIDAC FT-IR spectrophotometer. The spectra were referenced to the 1028 cm⁻¹ band of a 0.05 mm thick polystyrene film. UV-visible spectra were recorded on either Varian Cary-14 or Shimadzu M-20 spectrophotometer. Proton magnetic resonance spectra were obtained with a Varian Gemini-200 spectrometer using solutions in CDCl₃ referenced to tetramethylsilane. Elemental analyses data were obtained through Advanced Analytic Center in Korea Institute of Science and Technology (KIST). Mass spectral data were obtained by the LSIM technique at the Analytical Services Laboratory of Northwestern University.

Preparation of Para-Substituted Tetraphenylporphyrins, H₂(p-TPP), X=MeO, H, NO₂, F, Cl. In a typical procedure, 3.62 mL of pyrrole (5.40 × 10⁻² mole) and 8.35 g of p-chlorobenzaldehyde (5.94 × 10⁻² mole) in 200 mL of propionic acid were mixed and heated at reflux for 2 hr. The solution was allowed to cool slowly to room temperature during which time purple crystals precipitated. The crystals were collected by filtration, washed with methanol and hot water, and allowed to air-dry. This crystalline material, which was contaminated with small amounts of meso-tetraphenylchlorin (TPC), was oxidized with tetrachloro-1,4-benzoquinone in chloroform followed by separation with an alumina chromatography and crystallized with chloroform and methanol. The absorption spectrum of a CHCl₃ solution of the product was consistent with formation of the resulting 5,10,15,20-tetrakis(p-chlorophenyl)porphyrin.⁵⁻⁷ Anal. Calcd for C₄₄H₂₆N₄Cl₄: C, 70.2; H, 3.46; N, 7.45. Found: C, 70.0; H, 3.26; N, 7.21. All the products were also identified by FT-IR spectroscopy, NMR spectrometer, and elemental analyses.

Preparation of Ru(p-XTPP)(CO) Complexes, X=MeO, H, Cl, F. In a typical experiment, 100 mg of Ru₃CO₁₂ (1.56 × 10⁻⁴ mole) and 104 mg of H₂TPP (1.69 × 10⁻⁴ mole) were mixed in a flask containing 80 mL of toluene under N₂ atmosphere. The mixed solution was heated under reflux for a day and then allowed to cool at room temperature. The solvent was then removed by using a rotary evaporator. The solid remaining in the flask was dissolved in CHCl₃ and added to a silica gel column developed in CHCl₃. The final solution was evaporated to dryness and the resulting product was crystallized with chloroform and methanol. The IR spectrum contains a strong absorption at 1944 cm⁻¹ confirming the presence of a carbonyl ligand. The UV-visible spectrum of the product was consistent with formation of Ru(TPP)(CO).⁵⁻⁷ Anal. Calcd for C₄₅H₂₈N₄ORu·H₂O: C, 71.2; H, 3.95; N, 7.39. Found: C, 71.5; H, 3.91; N, 7.35. All the products were also identified by FT-IR spectroscopy, NMR spectrometer, and elemental analyses.

Preparation of Ru(p-XTPP)(CO)(Y) Complexes, X=MeO, H, Cl, F, Y=Pyridine, Imidazole, 1-Methylimidazole, 1,2-Dimethylimidazole. In a typical experiment, 50 mg of Ru(TPP)(CO) (0.068 mmole) and 12 mg of 1-Methylimidazole (0.146 mmole) were dissolved in CH₂Cl₂. After stirring at room temperature for an hour, the residue was evaporated to dryness. The reaction was judged by a change

Table 1. Carbonyl stretching frequencies (± 1 cm⁻¹)^a for Ru(p-XTPP)(CO)(X=H, OMe, Cl, and F) and Ru(p-XTPP)(CO)(Y)(Y=Py, Im, 1-MeIm, and 1,2-Me₂Im) complexes

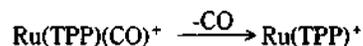
Compound Y ^b	Ru(p-MeOTPP) (CO)(Y)	Ru(TPP) (CO)(Y)	Ru(p-ClTPP) (CO)(Y)	Ru(p-FTPP) (CO)(Y)
NO	1941	1944	1948	1956
Py	1946	1950	1954	1956
Im	1938	1948	1950	1944
1-MeIm	1939	1941	1946	1950
1,2-Me ₂ Im	1941	1950	1948	1952

^adetermined in KBr. ^bNO, no coordinated nitrogen bases; Py, pyridine; Im, imidazole; 1-MeIm, 1-methylimidazole; 1,2-Me₂Im, 1,2-Dimethylimidazole.

in color to a more intense red. The product was separated by a column chromatography on silica gel with CHCl₃ as eluent. The leading band was collected and evaporated to dryness. The product was crystallized with CHCl₃ and MeOH. UV/vis (CHCl₃) λ_{max} (logε) 413 (4.4), 534 (3.8), 568 (3.2) nm; FT-IR (KBr) ν(CO) 1939 cm⁻¹; MS calc. for C₄₉H₃₄N₆ORu m/z 824; found m/z 824 (Ru(TPP)(CO)(1-MeIm)⁺), m/z 796 (Ru(TPP)(1-MeIm)⁺), m/z 714 (Ru(TPP)⁺); ¹H NMR (CHCl₃): δ 2.06 (3H, s, 1-MeIm CH₃), 4.58 (1H, s, 1-MeIm CH), 7.22 (10H, m, 1-MeIm CH and aromatic CH), 7.74 (8H, m, aromatic CH), 8.16 (4H, m, aromatic CH), 8.66 (8H, d, pyrrole CH). All the other products were also identified by UV/vis spectrophotometer, FT-IR spectroscopy, NMR spectrometer, Mass spectrometer, and elemental analyses.

Results and Discussions

Metalloporphyrins were obtained by modifications of the procedures of Tsutsui.¹ Their absorption maxima are similar to those previously reported.¹⁵⁻⁷ The mass spectra of Ru(TPP)(CO)(1-MeIm) showed peaks for Ru(TPP)(CO)(1-MeIm)⁺, Ru(TPP)(1-MeIm)⁺, and Ru(TPP)⁺ but not for Ru(TPP)(CO)⁺ as reported previously.¹² A metastable peak corresponding to



was observed for 5-coordinated Ru(TPP)(CO) complex. The mass spectral patterns of the 5- and 6-coordinated ruthenium carbonyl porphine complexes demonstrate that carbon monoxide initially dissociates from the parent ion. Due to the poor solubility of H₂(p-NO₂-TPP) in nonpolar solvents, Ru(p-NO₂-TPP)(CO) complex couldn't be prepared.

The carbonyl stretching frequencies for the 5- and 6-coordinated ruthenium porphine complexes are listed in Table 1. The data show that the stretching frequencies of the derivatives of ruthenium complexes are shifted slightly from those of the parent tetraphenylporphine compound. The average shift ~6 cm⁻¹ to lower wavenumber is observed as the electron donating ability of the substituent on the phenyl ring increases. For electron withdrawing substituents, there is ~7-12 cm⁻¹ shift to higher energy. The substituents bound to the phenyl ring in the porphine have a quantitative effect on the strength of carbon monoxide of Ru-CO bond.

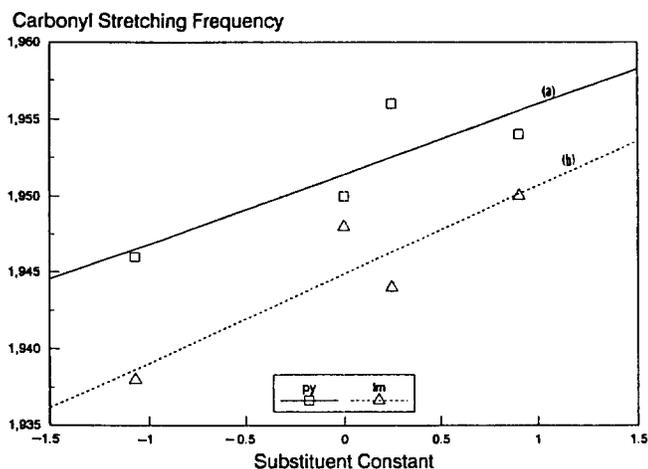


Figure 1. Plot of carbonyl stretching frequencies ($\pm 1 \text{ cm}^{-1}$) for (a) $\text{Ru}(p\text{-XTTP})(\text{CO})(\text{py})$ and (b) $\text{Ru}(p\text{-XTTP})(\text{CO})(\text{Im})$ vs. the Hammett substituent constant. Data are partially taken from Table 1.

On the other hand, the position of the emission wavelength maximum shifted to higher energy as the electron donor ability of the substituent on the phenyl ring increases.¹⁶

Ruthenium-carbonyl compounds were also obtained by the reaction of RuCl_3 and TPP under carbon monoxide bubbling.¹⁷ The prepared $\text{Ru}(\text{TPP})(\text{CO})(\text{Cl})$ complex have a carbonyl stretching frequency of 1993 cm^{-1} . The usual CO stretching for the +3 oxidation state of ruthenium as demonstrated in $\text{Ru}(\text{TPP})(\text{CO})(\text{Cl})$ shows the expected trend of greater back bonding for the lower oxidation state, as shown by the lower CO stretching for Ru(II) as compared to the Ru(III).

Figure 1 shows the relationship between $\nu(\text{CO})$ and Hammett σ values¹⁸ (vs. 4 σ here for the 4 substituents per porphyrin). Similar trends are observed for the ruthenium complexes containing other axial ligands. A straight line indicates that the relationship is more or less valid and partially reflects an electronic effect of the phenyl ring substituents in the porphyrin on the ruthenium metal center. As increasing the electron density of derivatives of *meso*-tetraphenylporphyrines, the stretching frequencies of carbonyl bonds decrease. However, the carbonyl stretching frequency of ruthenium complexes varies essentially randomly as the change of the basicity of axial 6th ligand. The shift of Soret band is not consistent with changing the porphyrin ligand.

Although there are insufficient data to draw quantitative conclusions, an important consideration in the correlation between the strength of the carbon monoxide in Ru-CO and the electronic properties of the *para* substituents of the porphyrin systems can be obtained. The evidence may be partially related to the fact that the four equivalent Ru-Neq(pyrrole) distance average to 2.058 \AA is shorter than the axial Ru-Nax (1-MeIm) bond distance (2.187 \AA).¹⁴ Gross *et al.*¹⁹ found that the phenyl ring substituents had about twice the effect on the electrochemical reduction of the π system than it had on the oxidation of the pyrrolic nitrogen lone pair from the study of the dependence of $E_{1/2}$ on Hammett σ values using the electrochemistry of synthetic, substituted porphyrins and

metalloporphyrins. On the other hand, the position of the emission wavelength maximum shifted to higher energy as the electron donor ability of the substituent on the phenyl ring increases.¹⁶

As conclusion, the carbonyl stretching frequencies for the 5- and 6-coordinated ruthenium carbonyl porphyrin complexes show that they are shifted slightly from those of the parent complex. Our results indicates the stretching frequencies of carbonyl bonds are sensitive to changes in the electron density of *meso*-tetraphenylporphyrines' derivatives rather than those in the basicity of the axial ligands.

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