

From this table, one can see that the dissociation of CO_2 is increased as the discharge current increases in the range of 10-14 mA and as the total pressure decreases in the range of 8-16 torr. Under our experimental conditions, the degree of CO_2 dissociation has a range of 18% to only 6%. As a whole, the catalytic electrode effect of $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ can be set in order of $0.050 > 0.025 > 0.075 > 0.100$ for x value.

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Preparation and T_1 Measurements of $\text{WH}_6(\text{PPh}_3)_3$

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The transition metal polyhydrides has been intensively investigated due to their interesting chemical reactivity (e.g. C-H activation)¹⁻³ and the possible existence of molecular

dihydrogen ligands⁴⁻⁶ in these complexes. The $\eta^2\text{-H}_2$ coordination appears to be sensitive for coordinated phosphine ligands. While $[\text{Mo}(\text{CO})(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2\text{H}_2]$ is characterized as a dihydrogen complex, the more basic $[\text{Mo}(\text{CO})(\text{tBu})_2\text{PC}_2\text{H}_4\text{P}(\text{tBu})_2\text{H}_2]$ is a dihydride.⁷

To our knowledge, among known tungsten polyhydrides no complexes supported by triphenylphosphine (PPh_3) ligand has been reported. Since PPh_3 ligand is bulky and relatively less basic, dissociation of this ligand is frequently observed to give the intermediate which easily reacts with substrates. Thus, the polyhydrides containing PPh_3 ligand is expected to be a better possible precursor to react, ligand deficient intermediate. To explore the chemistry of the tungsten polyhydride containing PPh_3 ligand, the tungsten polyhydrides, $\text{WH}_6(\text{PPh}_3)_3$ were prepared and the nature of hydride ligands was investigated by T_1 measurements on various temperatures.

Preparation and Characterization of $\text{WH}_6(\text{PPh}_3)_3$

Previous works show that high yield preparations of the type WH_4L_4 and WH_6L_3 ($\text{L} = \text{phosphine}$)⁸⁻⁹ are rare. The most common method of preparing the complexes, WH_4L_4 and WH_6L_3 is the reaction of WCl_6 or $\text{WCl}_4(\text{PR}_3)_2$ ($\text{PR}_3 = \text{PMe}_3$, PMe_2Ph , $\text{P}(i\text{-Pr})_3$) with hydride donor reagents (e.g. NaBH_4 , LiAlH_4) or $\text{Na}/\text{Hg}/\text{H}_2$ in the presence of excess tertiary phosphines. The yields of tungsten polyhydrides depends on hydride reagents, tertiary phosphines and reaction temperatures. The tungsten hexahydride, $\text{WH}_6(\text{PPh}_3)_3$ can be prepared by the interaction of $\text{WCl}_4(\text{PPh}_3)_2$ with NaBH_4 in the presence of excess PPh_3 . The yield of the product is moderate, ca. 43.4%. The product is slowly decomposed in solution when exposed to air. Although an excess PPh_3 was employed in the reaction mixture, the tungsten tetrahydride, $\text{WH}_4(\text{PPh}_3)_4$ is not formed, suggesting that the maximum coordination number of PPh_3 in this molecule is 3 as expected by large cone angle of PPh_3 (145°). The reaction product, $\text{WH}_6(\text{PPh}_3)_3$ is characterized by elemental analysis, ^1H , ^{31}P NMR and IR spectroscopy. In the ^1H NMR spectrum of the product the protons bound to tungsten appear as a quartet at -0.33 ppm due to the coupling with three equivalent phosphorus atoms (Figure 1a). The satellites due to splitting by ^{183}W ($J = 1/2$, 14% natural abundance) is also observed. The proton coupled ^{31}P NMR spectrum of the product shows a heptet for the phosphorus atoms (Figure 1b). This suggests that the tungsten is coordinated to six hydride ligands. The infrared spectrum of the product shows absorptions in the region of $1850\text{-}1769$ cm^{-1} in KBr disc assignable to the W-H stretchings. Similarly, the complexes, $\text{WH}_4(\text{PR}_3)_4$ ($\text{PR}_3 = \text{PMe}_2\text{Ph}$, PMePh_2) also shows absorptions as complex pattern in the region $1850\text{-}1700$ cm^{-1} of the IR spectrum.¹⁰

T_1 measurements. To investigate the nature of hydride ligands, T_1 measurements of hydride ligands were performed at various temperatures. The hydride region of the variable temperature ^1H NMR spectra of the hexahydride, $\text{WH}_6(\text{PPh}_3)_3$ in THF-d_3 at 300 MHz is shown in Figure 2. The hydrides peak is not separated to give other resonances in the investigated temperature range from 300 K to 200 K. This behavior is contrasted with that of analogous hexahydride containing a chelating triphosphine ligand, $\text{WH}_6(\text{PPh}_3(\text{CH}_2\text{CH}_2\text{PPh}_2)_2)_2$, which shows two hydride resonances at 243 K.¹¹ This is expected by the fact that a chelating ligand can slow down fluxionality in the resulting complex. T_1 values of hydride

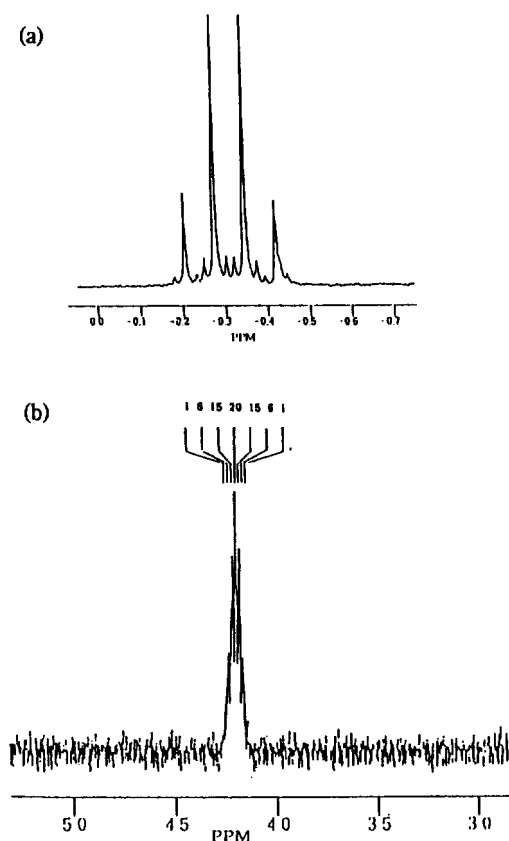


Figure 1. (a) The ^1H NMR spectrum of $\text{WH}_6(\text{PPh}_3)_3$ in the metal-hydride region in C_6D_6 . (b) The proton coupled ^{31}P NMR spectrum of $\text{WH}_6(\text{PPh}_3)_3$ in C_6D_6 .

resonances in ^1H NMR have been used in determining whether hydride complexes contain a molecular hydrogen ligand ($\eta^2\text{-H}_2$) or classical hydride ligand.¹² T_1 values in the hydride resonance of the complex, $\text{WH}_6(\text{PPh}_3)_3$ are decreased from 237 ms at 300 K to 147 ms at 220 K and increased to 221 ms at 200 K. Thus T_1 minimum value of the hydride resonance is 147 ms at 220 K. This relatively high $T_1(\text{min})$ value observed suggests that six hydride ligands in the $\text{WH}_6(\text{PPh}_3)_3$ is classical hydride. This $T_1(\text{min})$ value can be compared to those (103 and 126 ms) of $\text{WH}_6(\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2)_2$, which contains classical six hydride ligands.¹³

Thermolysis behavior of $\text{WH}_6(\text{PPh}_3)_3$. The thermal property of the $\text{WH}_6(\text{PPh}_3)_3$ is interesting on finding whether hydrides or triphenylphosphine ligands is dissociated. A sealed NMR tube containing the complex, $\text{WH}_6(\text{PPh}_3)_3$ and benzene- d_6 was heated at 80 $^\circ\text{C}$ for 12 h. The ^1H NMR spectrum of this sample shows that two of new hydride resonances appear at *ca.* -1.0 ppm as a broad feature and at *ca.* -4.4 ppm as a triplet of doublet ($J(\text{P-H})=45$ Hz, $J(\text{H-H})=5.9$ Hz) with a satellite peaks. The ^{31}P NMR spectrum shows that $\text{WH}_6(\text{PPh}_3)_3$ loses PPh_3 to give several species. The major product appears to be the ($\eta^6\text{-C}_6\text{D}_6$) $\text{WH}_2(\text{PPh}_3)_2$ which is an 18 electron molecule formed by the interaction of benzene- d_6 after extrusion of the four hydrides and PPh_3 ligands. The formulation of this molecule is supported by ^1H . In this structure the hydride resonance must show triplet for the coupling of two equivalent phosphorus atoms and split fur-

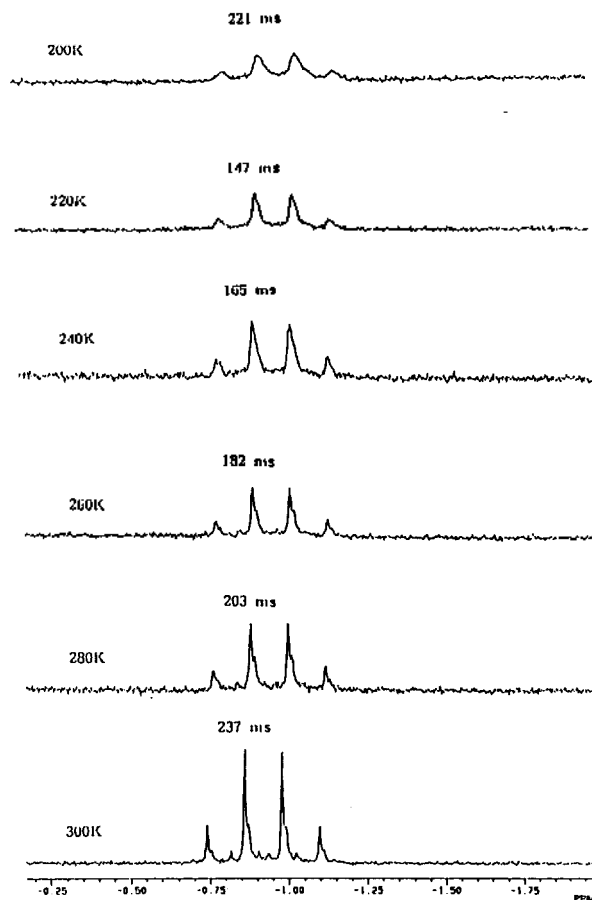
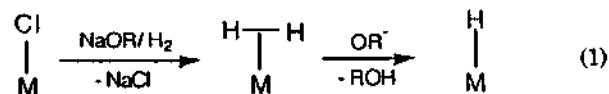


Figure 2. Variable-temperature ^1H NMR spectra (300 MHz, THF-d_6) of $\text{WH}_6(\text{PPh}_3)_3$ in the metal-hydride region. The T_1 values are written on the peaks.

ther due to other hydride ligand in ^1H NMR. This observation suggest that $\text{WH}_6(\text{PPh}_3)_3$ could be a good precursor to give a reactive species which reacts further with a variety of substrates.

Attempt to improve the yield of $\text{WH}_6(\text{PPh}_3)_3$. Since the complex, $\text{WH}_6(\text{PPh}_3)_3$ is prepared with moderate yield, we tried to develop new method. Recently, Morris *et al.*¹⁴ shows that heterolytic cleavage of dihydrogen provides a convenient route to the complexes of $\text{MH}_2(\text{PR}_2)_2$ ($\text{R}=\text{Et}$, $\text{M}=\text{Fe}$, Os ; $\text{R}=\text{Ph}$, $\text{M}=\text{Ru}$, Os) which are quite difficult to prepare by using standard hydride reagent, LiAlH_4 (Equation 1).



The reaction of $\text{WCl}_4(\text{PPh}_3)_2$ with NaOMe in the presence of excess PPh_3 under H_2 gas was unsuccessful; no metal hydride complexes were detected. This suggest that the π -donation ability of $\text{W}(\text{IV})$ complex is not enough to interact with molecular hydrogen.

Experimental

Methods and Materials. All manipulations were car-

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, $Ru(p\text{-XTPP})(CO)(\text{Nitrogenous Base})$ ($X = \text{MeO, NO}_2, \text{F, and Cl}$, 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