

# Preparation and characterization of $[\text{Re}(\text{bpy})(\text{CO})_3\text{L}][\text{SbF}_6]$ ( $\text{L} = \text{phosphine, phosphite}$ )

Hisao Hori <sup>a,\*</sup>, Kazuhide Koike <sup>a</sup>, Masakazu Ishizuka <sup>a</sup>, Koji Takeuchi <sup>a</sup>, Takashi Ibusuki <sup>a</sup>,  
Osamu Ishitani <sup>b</sup>

<sup>a</sup> Photoenergy Application Laboratory, National Institute for Resources and Environment, 16-3 Onogawa, Tsukuba, Ibaraki 305, Japan

<sup>b</sup> Graduate School of Science and Technology, Saitama University, 255 Shimo-Okubo, Urawa 338, Japan

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## Abstract

A series of rhenium complexes  $[\text{fac-Re}(\text{bpy})(\text{CO})_3\text{L}][\text{SbF}_6]$  ( $\text{bpy} = 2,2'$ -bipyridine,  $\text{L} = \text{P}(\text{nBu})_3, \text{PEt}_3, \text{PPh}_3, \text{P}(\text{OMe})\text{Ph}_2, \text{P}(\text{O}^i\text{Pr})_3, \text{P}(\text{OEt})_3, \text{P}(\text{OMe})_3, \text{P}(\text{OPh})_3$ ) has been prepared and characterized by the IR, UV-vis,  $^1\text{H}$  NMR,  $^{31}\text{P}$  NMR, X-ray photoelectron spectroscopy and electrochemical techniques. Variations in the electronic properties, i.e. CO stretching, metal-to-ligand charge transfer transition, and  $^{31}\text{P}$  NMR chemical shifts were interpreted on the basis of the electron-acceptor strength of  $\text{L}$ . However, the redox potential corresponding to  $[\text{Re}(\text{bpy})(\text{CO})_3\text{L}]^+ / [\text{Re}(\text{bpy})(\text{CO})_3\text{L}]$  showed 'V-character type' changes after the increase in the electron-acceptor strength of  $\text{L}$ . Variation of the P(2p) binding energy of the phosphorus atom indicated that the electronic structure of the coordinated phosphorus atom was strongly influenced by the electronic properties of the directly attached substituents.

**Keywords:** Rhenium complex; Phosphorus ligand; Carbonyl; Bipyridine

## 1. Introduction

Rhenium bipyridine complexes such as  $\text{fac-Re}(\text{bpy})(\text{CO})_3\text{X}$  ( $\text{bpy} = 2,2'$ -bipyridine,  $\text{X} = \text{Cl}, \text{Br}$ ) have received a great deal of attention because they can act as photo- and electrocatalysts for the reduction of  $\text{CO}_2$  to  $\text{CO}$  [1–4]. In particular, the complexes containing phosphorus ligands are of great importance because some of them show highly efficient photocatalysis for  $\text{CO}_2$  reduction [3,4]. To develop efficient catalysts, elucidation of their electronic structure is necessary because the catalysis is closely related to the electronic structure, e.g. the electron density on the metal center [5]. Up to now, only a few reports have described the spectroscopic data of rhenium bipyridine complexes containing phosphorus [4,6,7]. However, these reports were only concerned with the photoexcitation [4,6] or electrochemical [7] behavior of these complexes. There are no reported studies involving the systematic variation of the phosphorus ligand on rhenium bipyridine complexes. In the present work, we prepared eight

complexes containing phosphorus ligands, i.e.  $[\text{fac-Re}(\text{bpy})(\text{CO})_3\text{L}][\text{SbF}_6]$  ( $\text{L} = \text{P}(\text{nBu})_3, \text{PEt}_3, \text{PPh}_3, \text{P}(\text{OMe})\text{Ph}_2, \text{P}(\text{O}^i\text{Pr})_3, \text{P}(\text{OEt})_3, \text{P}(\text{OMe})_3, \text{P}(\text{OPh})_3$ ). The effects of the electron-acceptor strength of axial ligand  $\text{L}$  on the electronic structure of central rhenium(I), CO and bpy ligands were investigated by the IR, UV-vis absorption/emission,  $^1\text{H}$  NMR,  $^{31}\text{P}$  NMR, X-ray photoelectron spectroscopy (XPS) and electrochemical techniques.

## 2. Experimental details

### 2.1. Materials

Reagents and solvents of commercially high purity were obtained from Wako Pure Chemical Industries, Kanto Chemical Co. Inc., and Aldrich Chemical Company. MeCN was distilled over  $\text{CaH}_2$ . All solvents were deoxygenated prior to use with dry argon.  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{MeCN})][\text{SbF}_6]$  was prepared from  $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$  according to a literature method [6] with the following modifications.  $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$  (1.18 g, 2.55 mmol) and  $\text{AgSbF}_6$  (2.4 g, 7.0 mmol) were

\* Corresponding author.

heated at reflux in MeCN (100 ml) under an argon atmosphere for 8 h. After cooling, the solution was filtered and evaporated to dryness. The product was dissolved in a 1:1:1 ethanol–acetone–water mixture (50 ml) and recrystallized through the slow removal of the solvent under vacuum. Repeated recrystallization gave  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{MeCN})][\text{SbF}_6]$  (1.48 g, 2.10 mmol). Yield: 82.4%.

### 2.2. Preparation of $[\text{Re}(\text{bpy})(\text{CO})_3\text{P}(\text{nBu})_3][\text{SbF}_6]$ (1)

This complex was prepared using the method for  $[\text{Re}(\text{bpy})(\text{CO})_3\text{PMe}_3][\text{PF}_6]$  [6] with the following modifications.  $[\text{Re}(\text{bpy})(\text{CO})_3(\text{MeCN})][\text{SbF}_6]$  (0.20 g, 0.28 mmol) and  $\text{P}(\text{nBu})_3$  (3.0 g, 14.8 mmol) were dissolved into THF (40 ml). The solution was heated at reflux under an argon atmosphere for 8 h in a dim light. After cooling to room temperature, the solution was evaporated to dryness and recrystallized from  $\text{CH}_2\text{Cl}_2$ – $\text{Et}_2\text{O}$  to give  $[\text{Re}(\text{bpy})(\text{CO})_3\text{P}(\text{nBu})_3][\text{SbF}_6]$  (1) (0.15 g, 0.18 mmol).  $^1\text{H}$  NMR: 8.96 (d,  $J = 5.5$  Hz, 2H, bpy-6,6'), 8.72 (d,  $J = 8.4$  Hz, 2H, bpy-3,3'), 8.34 (dd,  $J = 7.6, 8.4$  Hz, 2H, bpy-4,4'), 7.63 (dd,  $J = 5.5, 7.6$  Hz, 2H, bpy-5,5'), 1.29–1.34 (m, 6H,  $\text{P}-\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.16–1.20 (m, 12H,  $\text{P}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 0.83 (t,  $J = 6.8$  Hz, 9H,  $\text{P}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ). Yield: 63.1%. Anal. Found: C, 34.51; H, 4.02; N, 3.08.  $\text{C}_{25}\text{H}_{35}\text{F}_6\text{N}_2\text{O}_3\text{PReSb}$ . Calc.: C, 34.73; H, 4.08; N, 3.24%.

### 2.3. Preparation of $[\text{Re}(\text{bpy})(\text{CO})_3\text{PEt}_3][\text{SbF}_6]$ (2)

This method is almost identical to that of 1 except that  $\text{PEt}_3$  was used.  $^1\text{H}$  NMR: 8.97 (d,  $J = 5.6$  Hz, 2H, bpy-6,6'), 8.69 (d,  $J = 8.4$  Hz, 2H, bpy-3,3'), 8.32 (dd,  $J = 7.4, 8.4$  Hz, 2H, bpy-4,4'), 7.65 (dd,  $J = 5.6, 7.4$  Hz, 2H, bpy-5,5'), 1.35–1.45 (m, 6H,  $\text{PCH}_2\text{CH}_3$ ), 0.84–0.95 (m, 9H,  $\text{PCH}_2\text{CH}_3$ ). Yield: 90.6%. Anal. Found: C, 29.03; H, 2.95; N, 3.36.  $\text{C}_{19}\text{H}_{23}\text{F}_6\text{N}_2\text{O}_3\text{PReSb}$ . Calc.: C, 29.24; H, 2.97; N, 3.59%.

### 2.4. Preparation of $[\text{Re}(\text{bpy})(\text{CO})_3(\text{PPh}_3)][\text{SbF}_6]$ (3)

This method is almost identical to that of 1 except that  $\text{PPh}_3$  was used.  $^1\text{H}$  NMR: 8.54 (d,  $J = 8.0$  Hz, 2H, bpy-3,3'), 8.34 (d,  $J = 5.5$  Hz, 2H, bpy-6,6'), 8.13 (dd,  $J = 7.4, 8.0$  Hz, 2H, bpy-4,4'), 7.10–7.40 (m, 17H, bpy-5,5', Ph). Yield: 73.9%. Anal. Found: C, 39.98; H, 2.19; N, 2.78.  $\text{C}_{31}\text{H}_{23}\text{F}_6\text{N}_2\text{O}_3\text{PReSb}$ . Calc.: C, 40.27; H, 2.51; N, 3.03%.

### 2.5. Preparation of $[\text{Re}(\text{bpy})(\text{CO})_3\{\text{P}(\text{OMe})\text{Ph}_2\}][\text{SbF}_6]$ (4)

This method is almost identical to that of 1 except that  $\text{P}(\text{OMe})\text{Ph}_2$  was used.  $^1\text{H}$  NMR: 8.65 (d,  $J =$

5.2 Hz, 2H, bpy-6,6'), 8.34 (d,  $J = 8.3$  Hz, 2H, bpy-3,3'), 8.17 (dd,  $J = 7.7, 8.3$  Hz, 2H, bpy-4,4'), 7.49–7.54 (m, 4H, Ph-*meta*), 7.44 (dd,  $J = 5.2, 7.7$  Hz, 2H, bpy-5,5'), 7.35–7.40 (m, 2H, Ph-*para*), 7.10–7.15 (m, 4H, Ph-*ortho*), 3.15 (d,  $J_{\text{H,P}} = 11.8$  Hz, 3H,  $\text{POCH}_3$ ). Yield: 89.4%. Anal. Found: C, 35.30; H, 2.26; N, 2.97.  $\text{C}_{26}\text{H}_{21}\text{F}_6\text{N}_2\text{O}_4\text{PReSb}$ . Calc.: C, 35.55; H, 2.41; N, 3.19%.

### 2.6. Preparation of $[\text{Re}(\text{bpy})(\text{CO})_3\text{P}(\text{O}^i\text{Pr})_3][\text{SbF}_6]$ (5)

This method is almost identical to that of 1 except that  $\text{P}(\text{O}^i\text{Pr})_3$  was used.  $^1\text{H}$  NMR: 8.89 (d,  $J = 5.6$  Hz, 2H, bpy-6,6'), 8.72 (d,  $J = 8.3$  Hz, 2H, bpy-3,3'), 8.34 (dd,  $J = 7.5, 8.3$  Hz, 2H, bpy-4,4'), 7.64 (dd,  $J = 5.6, 7.5$  Hz, 2H, bpy-5,5'), 4.42–4.49 (m, 3H,  $\text{POCH}\{\text{CH}_3\}_2$ ), 1.05 (d,  $J = 6.1$  Hz, 18H,  $\text{POCH}\{\text{CH}_3\}_2$ ). Yield: 67.1%. Anal. Found: C, 30.01; H, 3.25; N, 2.92.  $\text{C}_{22}\text{H}_{29}\text{F}_6\text{N}_2\text{O}_6\text{PReSb}$ . Calc.: C, 30.36; H, 3.36; N, 3.22%.

### 2.7. Preparation of $[\text{Re}(\text{bpy})(\text{CO})_3\text{P}(\text{OEt})_3][\text{SbF}_6]$ (6)

This method is almost identical to that of 1 except that  $\text{P}(\text{OEt})_3$  was used.  $^1\text{H}$  NMR: 8.91 (d,  $J = 5.5$  Hz, 2H, bpy-6,6'), 8.66 (d,  $J = 8.2$  Hz, 2H, bpy-3,3'), 8.31 (dd,  $J = 7.6, 8.2$  Hz, 2H, bpy-4,4'), 7.64 (dd,  $J = 5.5, 7.6$  Hz, 2H, bpy-5,5'), 3.82 (quintet,  $J_{\text{H,P}}, J = 7.0$  Hz, 6H,  $\text{POCH}_2\text{CH}_3$ ), 1.06 (t,  $J = 7.0$  Hz, 9H,  $\text{POCH}_2\text{CH}_3$ ). Yield: 85.2%. Anal. Found: C, 27.38; H, 2.60; N, 3.23.  $\text{C}_{19}\text{H}_{23}\text{F}_6\text{N}_2\text{O}_6\text{PReSb}$ . Calc.: C, 27.55; H, 2.80; N, 3.38%.

### 2.8. Preparation of $[\text{Re}(\text{bpy})(\text{CO})_3\text{P}(\text{OMe})_3][\text{SbF}_6]$ (7)

This method is almost identical to that of 1 except that  $\text{P}(\text{OMe})_3$  was used.  $^1\text{H}$  NMR: 8.92 (d,  $J = 5.7$  Hz, 2H, bpy-6,6'), 8.63 (d,  $J = 8.2$  Hz, 2H, bpy-3,3'), 8.32 (dd,  $J = 7.5, 8.2$  Hz, 2H, bpy-4,4'), 7.64 (dd,  $J = 5.7, 7.5$  Hz, 2H, bpy-5,5'), 3.49 (d,  $J_{\text{H,P}} = 11.0$  Hz, 9H,  $\text{POCH}_3$ ). Yield: 89.4%. Anal. Found: C, 24.64; H, 2.10; N, 3.49.  $\text{C}_{16}\text{H}_{17}\text{F}_6\text{N}_2\text{O}_6\text{PReSb}$ . Calc.: C, 24.44; H, 2.18; N, 3.56%.

### 2.9. Preparation of $[\text{Re}(\text{bpy})(\text{CO})_3\text{P}(\text{OPh})_3][\text{SbF}_6]$ (8)

This method is almost identical to that of 1 except that  $\text{P}(\text{OPh})_3$  was used.  $^1\text{H}$  NMR: 8.65 (d,  $J = 8.2$  Hz, 2H, bpy-3,3'), 8.58 (d,  $J = 5.3$  Hz, 2H, bpy-6,6'), 8.24 (dd,  $J = 7.4, 8.2$  Hz, 2H, bpy-4,4'), 7.38 (dd,  $J = 5.3, 7.4$  Hz, 2H, bpy-5,5'), 7.14–7.30 (m, 9H, Ph-*meta*–*para*), 6.82 (d,  $J = 8.2$  Hz, 6H, Ph-*ortho*). Yield: 88.2%. Anal. Found: C, 38.10; H, 2.33; N, 2.64.  $\text{C}_{31}\text{H}_{23}\text{F}_6\text{N}_2\text{O}_6\text{PReSb}$ . Calc.: C, 38.29; H, 2.38; N, 2.88%.

## 2.10. Physical measurements

IR and UV–vis absorption spectra were respectively recorded on Jeol JIR-6500 and Hitachi 330 spectrophotometers. Emission spectra at 25 °C were measured with a Hitachi F-3000 fluorescence spectrophotometer. To determine the quantum yields for emission, a solution (0.5 M H<sub>2</sub>SO<sub>4</sub>) of quinine bisulfate was used as the standard ( $\Phi = 0.546$ ) [8], after applying a correction for differing refractive indices of the solvents. Emission lifetime  $\tau_{em}$  was measured by the flash photolysis technique reported previously [4]. Cyclic voltammetry was made using a BAS 100B electrochemical analyzer in an MeCN solution containing the complex (0.5 mM) and a supporting electrolyte <sup>n</sup>Bu<sub>4</sub>NClO<sub>4</sub> (0.1 M) with a scanning rate of 100 mV s<sup>-1</sup>. A glassy carbon working electrode and an Ag/AgNO<sub>3</sub> reference electrode were used. The flow electrolytic method has been described in detail elsewhere [4]. <sup>1</sup>H NMR (300 MHz) and <sup>31</sup>P NMR (121 MHz) spectra were taken in CDCl<sub>3</sub> using the Bruker AC 300P system. The chemical shifts for <sup>31</sup>P NMR are relative to an external standard of 85% H<sub>3</sub>PO<sub>4</sub>. The plus sign was adopted for signals appearing at a lower magnetic field than the signal of the standard sample. X-ray photoelectron spectra for the regions corresponding to the binding energy of core electrons, Re(4f<sub>7/2</sub>), P(2p), N(1s) and F(1s) were taken at room temperature with a Shimadzu ESCA 750 instrument using Mg K $\alpha$  radiation. The samples were attached to the sample holder using conductive double-sided tape. The binding energy was referred to F(1s) peak (686.0 eV) as the internal standard because all of the complexes contained F atoms in the SbF<sub>6</sub><sup>-</sup> counter anion. F atoms are considered to be in almost the same environment because the counter anion is not directly bound to the rhenium(I). The measurements were carried out in as short a time as possible, because prolonged X-ray irradiation changed the samples from yellow to brown. For irradiation up to 10 min, no visual damage was found.

## 3. Results and discussion

### 3.1. Preparation and identification

The results of elemental analyses confirmed that all the complexes have a formula [Re(bpy)(CO)<sub>3</sub>L][SbF<sub>6</sub>]. Table 1 lists the CO stretching frequencies ( $\nu(\text{CO})$ ) of the complexes, together with Tolman's  $\chi$ , which is a measure for the electron-acceptor strength of the phosphorus ligands [9–11], and the cone angle, which is a measure of the steric bulkiness of the phosphorus ligands [9,11–13]. It should be pointed out that the phosphorus ligands used in this study have similar cone angles, except for PPh<sub>3</sub>. These complexes have three  $\nu(\text{CO})$  bands (2a', a'') as expected for the C<sub>s</sub> tricarbonyl moiety. This spectral pattern is almost identical with those of *fac*-Re(bpy)(CO)<sub>3</sub>Cl and *fac*-Re(bpy)(CO)<sub>3</sub>OC(O)H, of which the structures are confirmed by NMR, IR, and X-ray crystallography [2,14]. Therefore, it is confirmed that [Re(bpy)(CO)<sub>3</sub>L][SbF<sub>6</sub>] have the structure illustrated in Fig. 1.

### 3.2. IR spectra

Fig. 2 shows the plots of  $\nu(\text{CO})$  against  $\chi$ . Linear correlations with positive slopes were clearly observed for each  $\nu(\text{CO})$  band. These facts indicate that increasing the electron-acceptor strength of ligand L causes a decrease in the  $\pi$ -back donation from the rhenium(I) to the carbonyl ligands. In other words, the d <sub>$\pi$</sub> -electron density of the rhenium(I) decreases with an increase in the electron-acceptor strength of ligand L. The  $\chi$  values are based on the  $\nu(\text{CO})$  frequencies of Ni(CO)<sub>3</sub>L (L = phosphorus ligand) complexes having C<sub>3v</sub> symmetry [9–11]. In contrast, the present complexes have lower C<sub>s</sub> symmetry; nevertheless, a fairly good correlation was observed, as shown in Fig. 2, implying a wider validity of  $\chi$  as a measure of electron-acceptor strength.

Table 1  
 $\nu(\text{CO})$  frequencies for [Re(bpy)(CO)<sub>3</sub>L][SbF<sub>6</sub>] together with electronic and steric parameters for ligand L

No.	L	$\nu(\text{CO})$ (cm <sup>-1</sup> ) <sup>a</sup>			$\chi$ <sup>b</sup>	Cone angle (deg)	
		a'	a''	a'		Tolman's values <sup>c</sup>	Stahl's values <sup>d</sup>
1	P( <sup>n</sup> Bu) <sub>3</sub>	2037	1947	1920	5.25	132	
2	PEt <sub>3</sub>	2036	1947	1920	6.30	132	137
3	PPh <sub>3</sub>	2041	1955	1924	13.25	145	
4	P(OMe)Ph <sub>2</sub>	2043	1957	1928	16.30	132	
5	P(O <sup>i</sup> Pr) <sub>3</sub>	2045	1958	1924	19.05	130	
6	P(OEt) <sub>3</sub>	2047	1962	1927	21.60	109	134
7	P(OMe) <sub>3</sub>	2049	1965	1930	24.10	107	128
8	P(OPh) <sub>3</sub>	2059	1978	1942	30.20	128	

<sup>a</sup> Measured in an MeCN solution. <sup>b</sup> Taken from Ref. [9]; these are renewal values determined by FTIR, which are slightly different from Tolman's earlier data [10]. <sup>c</sup> Taken from Ref. [11]. <sup>d</sup> Taken from Ref. [12].

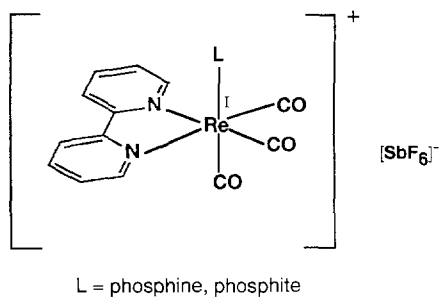


Fig. 1. Representation of the structure of  $[\text{Re}(\text{bpy})(\text{CO})_3\text{L}][\text{SbF}_6]$ .

### 3.3. Electrochemistry

The cyclic voltammogram (CV) of **2** is shown in Fig. 3. The first reduction is reversible, with a half-wave potential  $E_{1/2}$  of  $-1.39\text{ V}$ , and the second one is chemically irreversible, with peak potential  $E_p^c$  of  $-1.93\text{ V}$  (Fig. 3(a)). Fig. 4 shows the  $\nu(\text{CO})$  IR spectra recorded following flow-electrolysis of **2** with reduction potentials of 0 to  $-2.1\text{ V}$ . Generation of the reduced species is clearly observed. In this case, the number of electrons  $n$  per the complex reduced can be calculated using the following equation:

$$n = (i - i_b) / [2]_0 F v' = (5.5 \times 10^{-4} - 2.0 \times 10^{-4}) / [(5 \times 10^{-4}) \times 96480 \times (8.3 \times 10^{-6})] = 0.9$$

where  $i$  (A) is the current which is required for quantitative reduction of **2**,  $i_b$  (A) is the background current,  $[2]_0$  (M) is the initial concentration of **2**,  $F$  (C) is the Faraday constant, and  $v'$  ( $\text{s}^{-1}$ ) is the flow rate of the solution. The results show that the reduced species observed here must be one-electron reduced species of **2**, corresponding to the first reversible one-electron reduction in the CV. The three  $\nu(\text{CO})$  bands of this reduced species shifted down in frequency from **2** by 25, 35, and  $32\text{ cm}^{-1}$ . In earlier work, it was shown that similar shifts to low frequency ( $27$  and  $33\text{ cm}^{-1}$ ) occur on one-electron reduction of

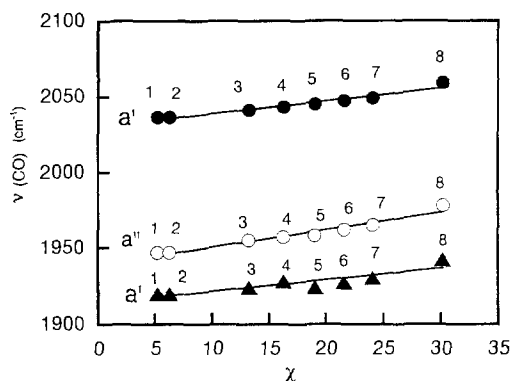


Fig. 2. Plots of three  $\nu(\text{CO})$  frequencies against  $\chi$ .

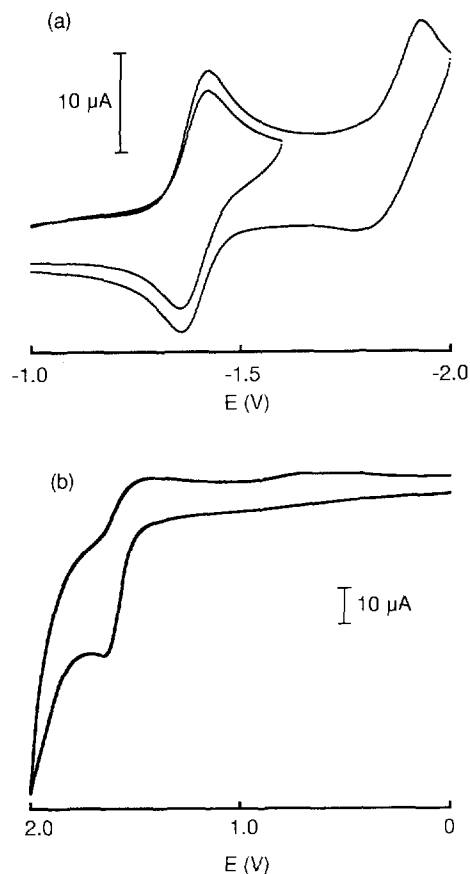


Fig. 3. CV of complex **2**: (a) reductive and (b) oxidative potential regions.

$[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_2\{\text{P}(\text{OEt})_3\}_2]^+$  to  $[\text{Re}^{\text{I}}(\text{bpy}^{\cdot-})(\text{CO})_2\{\text{P}(\text{OEt})_3\}_2]$ , of which an electron is located on the bpy ligand [4]. Consequently, the first

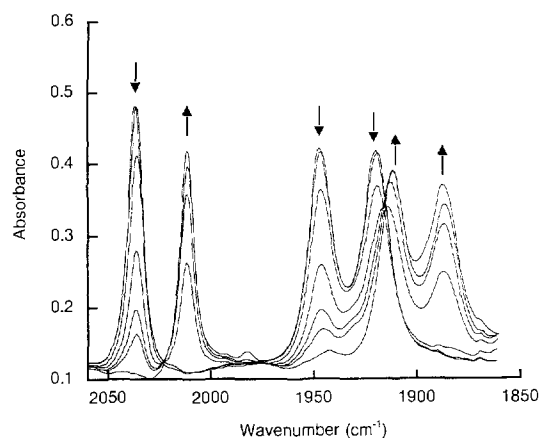


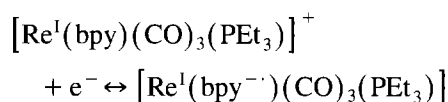
Fig. 4.  $\nu(\text{CO})$  IR spectra recorded following flow-electrolysis of **2** ( $0.5\text{ mM}$ ) in an Ar-saturated MeCN solution containing  $0.1\text{ M}$   $\text{Bu}_4\text{NClO}_4$ . The solution of **2** was reduced from 0 to  $-2.1\text{ V}$  at a constant flow rate of  $0.5\text{ ml min}^{-1}$ . The ohmic potential drop of the several hundred millivolts was observed between the reference and working electrodes. Downward arrows indicate loss of **2**; upward arrows show generation of the one-electron reduced species of **2**.

Table 2  
CV data for  $[\text{Re}(\text{bpy})(\text{CO})_3\text{L}][\text{SbF}_6]^\text{a}$

No.	L	$E_{1/2}$ (V)	$E_p^c$ (V)	$E_p^a$ (V)
1	$\text{P}(\text{nBu})_3$	-1.39	-1.94	1.6
2	$\text{PEt}_3$	-1.39	-1.93	1.6
3	$\text{PPh}_3$	-1.40	-1.70	1.6
4	$\text{P}(\text{OMe})\text{Ph}_2$	-1.43	-1.82	1.6
5	$\text{P}(\text{O}^i\text{Pr})_3$	-1.44	-1.89	1.7
6	$\text{P}(\text{OEt})_3$	-1.43	-1.87	1.7
7	$\text{P}(\text{OMe})_3$	-1.41	-1.84	1.8
8	$\text{P}(\text{OPh})_3$	-1.39	-1.77	1.9

<sup>a</sup> In an argon-saturated MeCN solution containing 0.1 M  $\text{nBu}_4\text{NClO}_4$ . A glassy carbon working electrode and an  $\text{Ag}/\text{AgNO}_3$  reference electrode were used. The scan rate was  $100\text{mVs}^{-1}$ .

reversible wave is one-electron, largely a ligand located process:



In contrast, the oxidation of **2** is characterized by a broad wave with a peak potential,  $E_p^a = 1.6\text{V}$  (Fig. 3(b)), in common with many reported rhenium bipyridine complexes which show a similar irreversible peak at a positive potential and which is attributed to the one-electron oxidation of rhenium(I) to rhenium(II) [15]. The cyclic voltammograms of the other complexes, **1** and **3–8**, are similar to that of **2** and the electrochemical data are summarized in Table 2.

The  $\chi$  dependence of the  $E_{1/2}$  is shown in Fig. 5. As mentioned above, the  $E_{1/2}$  directly reflects electron affinity of the bpy ligand and the  $\chi$  reflects the electron-acceptor strength of ligand L. It was expected that  $E_{1/2}$  would become more positive with increase in  $\chi$ . This is because increasing the electron-acceptor strength of ligand L causes a decrease in the  $d_\pi$ -electron density on the rhenium(I), which causes a decrease in the electron density on the bpy ligand. However, the relation between  $E_{1/2}$  and  $\chi$  is quite different from such expectation. It looks like a 'V-character'. This result suggests that the electron affinity of the bpy ligand is affected not merely by the electron density on the central Re(I) ion. Through-space interaction may occur between the bpy and L. In that case, the shape and direction of the orbitals of ligand L should be important. Work currently in progress involves an investigation into the through-space interaction, and that will be the subject of a future paper.

### 3.4. UV-vis absorption and emission spectra

The spectra of complex **1** are shown in Fig. 6. We assign the absorption around 356 nm to the metal (rhenium) to ligand (bpy) charge transfer (MLCT) band, and the broad emission around 532 nm is  $^3\text{MLCT}$  emis-

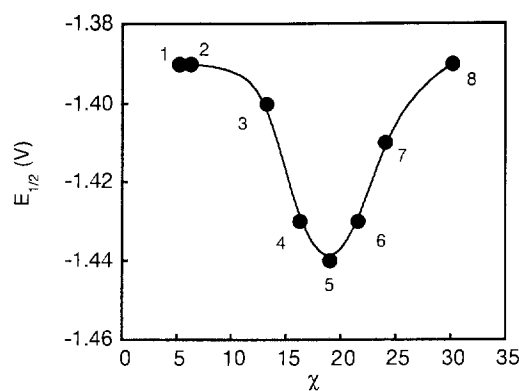


Fig. 5. Plots of  $E_{1/2}$  against  $\chi$ .

sion band, as a result of a comparison with the analogous rhenium complexes [4,6,16]. This is supported by the fact that the absorption band around 356 nm is solvent sensitive; a change in the solvent from MeCN to less polar  $\text{CH}_2\text{Cl}_2$  leads to a red-shift, as expected of the MLCT band. These complexes have two bands around 310–320 nm, which are insensitive to shifts with solvent. These bands are assigned to the  $\pi-\pi^*$  transitions in the bpy ligand, referring to the spectra of analogous rhenium complexes [17,18] and protonated bipyridine [19]. The UV-vis absorption and emission spectra of the other complexes are similar to **1** and are summarized in Table 3.

Fig. 7 shows the plots of the energy of the MLCT absorption and emission maxima,  $E_{\text{MLCT}}$  and  $E_{\text{em}}$ , against  $\chi$ . An increasing tendency of  $E_{\text{MLCT}}$  and  $E_{\text{em}}$  against  $\chi$  was observed, indicating that increasing the electron-acceptor strength of ligand L increases the MLCT transition energy. As the energy of the MLCT state is dominantly dependent on both the relative ease of oxidation of the rhenium(I) and that of reduction in the bpy ligand, it is not surprising that the energy of the MLCT state has a good correlation with  $E_p^a - E_{1/2}$  (see Section 3.3). Fig. 8 shows  $E_p^a - E_{1/2}$  against  $\chi$ ; it

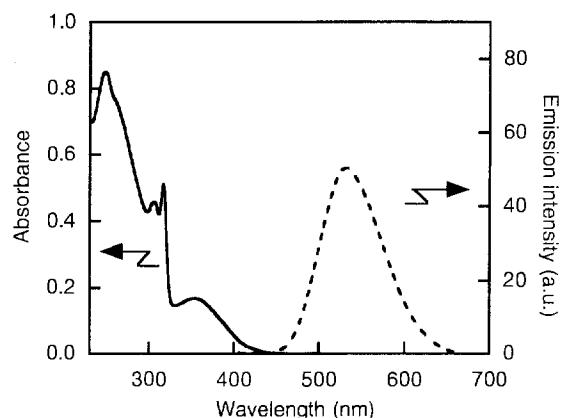


Fig. 6. UV-vis absorption and emission spectra for an MeCN solution of complex **1** ( $4.05 \times 10^{-5}\text{M}$ ).

Table 3  
UV-vis absorption and emission data for  $[\text{Re}(\text{bpy})(\text{CO})_3\text{L}][\text{SbF}_6]^\text{a}$

No.	L	$\lambda_{\text{ab}}$ (nm) ( $\epsilon/10^3$ ) ( $\text{M}^{-1} \text{cm}^{-1}$ )	$\lambda_{\text{em}}$ (nm)	$\Phi_{\text{em}}$	$\tau_{\text{em}}$ (ns)
1	$\text{P}(\text{nBu})_3$	255 (21.0), 309 (11.2), 320 (12.6), 356 (4.05)	532	0.034	621
2	$\text{PEt}_3$	249 (20.4), 308 (10.9), 319 (12.4), 354 (3.95)	530	0.063	654
3	$\text{PPh}_3$	251 <i>sh</i> (23.6), 312 (10.6), 322 (12.8), 354 <i>sh</i> (3.58)	517	0.053	416
4	$\text{P}(\text{OMe})\text{Ph}_2$	248 <i>sh</i> (25.0), 307 (10.7), 317 (12.6), 350 <i>sh</i> (3.39)	522	0.064	644
5	$\text{P}(\text{O}^i\text{Pr})_3$	245 (20.1), 306 (11.6), 315 (14.3), 346 <i>sh</i> (3.37)	521	0.071	952
6	$\text{P}(\text{OEt})_3$	249 (20.0), 307 (11.1), 317 (13.5), 351 <i>sh</i> (3.06)	522	0.088	1034
7	$\text{P}(\text{OMe})_3$	247 (23.9), 307 (11.0), 318 (13.4), 348 <i>sh</i> (3.01)	520	0.106	1076
8	$\text{P}(\text{OPh})_3$	244 (21.6), 308 (10.9), 317 (13.1), 343 <i>sh</i> (3.23)	505	0.120	958

<sup>a</sup> In an MeCN solution.

shows a similar  $\chi$  dependence to the MLCT energy (Fig. 7). Although  $E_{1/2}$  has the 'unusual'  $\chi$  dependence as seen in Fig. 5, the MLCT energy shows a 'normal' one because the variation in  $E_{1/2}$  with ligand L (ca. 50 mV) is much smaller than that of  $E_p^\text{a}$  (ca. 300 mV), i.e. the change in the oxidation potential of the central Re(I) ion mainly dominates the alternation in the MLCT state by the variation of L. It is of importance that the color of the complex changes by a variation of ligand L, because the first step of the photocatalytic reduction of  $\text{CO}_2$  using rhenium bipyridine complexes is excitation from the ground state to the MLCT state [1–4]. The quantum yields for the emission  $\Phi_{\text{em}}$  increase with increase in  $\chi$ , indicating that an increase in the electron-accepting strength of ligand L increases the  $\Phi_{\text{em}}$  values. These facts are consistent with the energy gap law [6]; an increase in the energy of an MLCT excited state decreases the non-radiative decay rate from it.

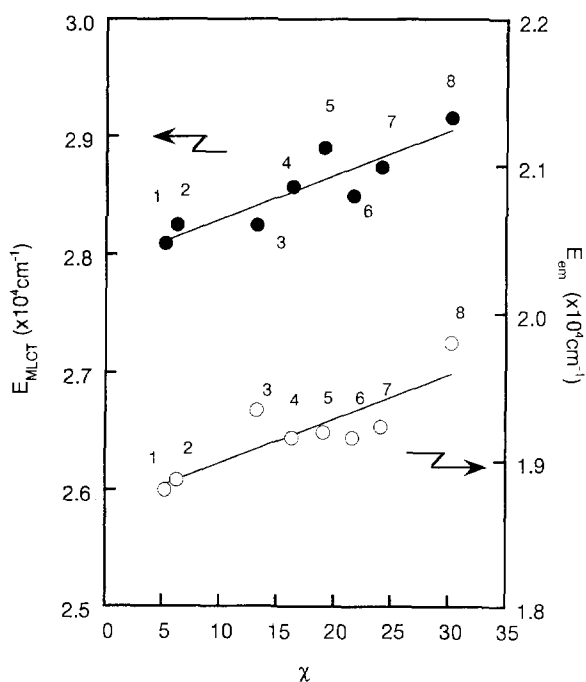


Fig. 7. Plots of  $E_{\text{MLCT}}$  and  $E_{\text{em}}$  against  $\chi$ .

As for the energy of the  $\pi-\pi^*$  absorption maxima, smaller and no systematic changes were observed, in contrast to the MLCT transition. This is because the effects of ligand L on bpy should be smaller than those on the central Re(I) ion, which is directly coordinated by L; also, through-space interaction may exist between bpy and some of the L ligands, depending on the structure of L.

### 3.5. $^1\text{H}$ NMR spectra

The effect of the variation in ligand L on the chemical shifts  $\delta_{\text{H}}$  for the protons on the bpy ligand is not large, and no significant tendency can be observed. In the case of 6,6'-bpy protons, the  $\delta_{\text{H}}$  values for complexes 3, 4, and 8, in which phenyl or phenoxy groups are directly attached to the phosphorus atom, deviate from those of other complexes, due to the large shielding effect of these groups.

### 3.6. $^{31}\text{P}$ NMR spectra

Table 4 lists the  $^{31}\text{P}$  NMR chemical shifts ( $\delta^{31}\text{P}$ ) of the complexes and corresponding free ligands. The coordination shifts  $\Delta\delta^{31}\text{P}$ , which are defined as  $\delta^{31}\text{P}(\text{complex}) - \delta^{31}\text{P}(\text{ligand})$ , are also listed. In most metal complexes having phosphorus ligands, the coordination shifts are positive [20–24]. However, in the

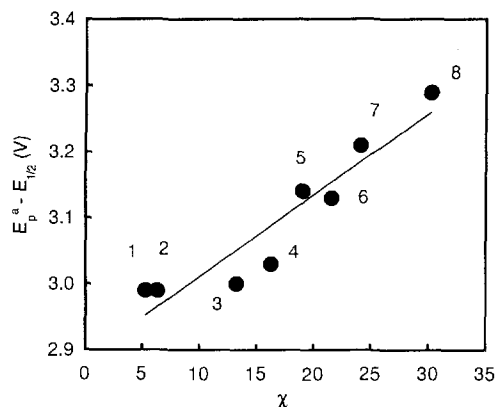


Fig. 8. Plots of  $E_p^\text{a} - E_{1/2}$  against  $\chi$ .

Table 4  
 $^{31}\text{P}$  NMR data for  $[\text{Re}(\text{bpy})(\text{CO})_3\text{L}][\text{SbF}_6]^\text{a}$

No.	L	Chemical shifts (ppm)		
		$\delta^{31}\text{P}$ (complex)	$\delta^{31}\text{P}$ (ligand)	$\Delta\delta^{31}\text{P}$ (complex – ligand)
1	$\text{P}(\text{n-Bu})_3$	-12.7	-31.1 <sup>b</sup>	18.4
2	$\text{PEt}_3$	-6.9	-17.7 <sup>b</sup>	10.8
3	$\text{PPh}_3$	15.3	-9.3	24.6
4	$\text{P}(\text{OMe})\text{Ph}_2$	104.0	113.1	-9.1
5	$\text{P}(\text{O}^i\text{Pr})_3$	101.4	135.5	-34.1
6	$\text{P}(\text{OEt})_3$	103.5	134.9	-31.4
7	$\text{P}(\text{OMe})_3$	108.1	133.5 <sup>b</sup>	-25.4
8	$\text{P}(\text{OPh})_3$	96.2	122.1 <sup>b</sup>	-25.9

<sup>a</sup> Measured in a  $\text{CDCl}_3$  solution; 85%  $\text{H}_3\text{PO}_4$  was used for the external standard. <sup>b</sup> Taken from Ref. [20].

present  $[\text{Re}(\text{bpy})(\text{CO})_3\text{L}][\text{SbF}_6]$ , complexes 4–8, which have ligands of larger  $\chi$  values, the coordination shifts were negative. The coordination shift is associated with electronic and/or steric changes accompanied with coordination [22,24]. The electronic change is caused by an electron drift resulting from the coordination. If the electron drift from the rhenium(I) to the phosphorus atom is large, a negative coordination shift is expected. In contrast, the steric change is mainly associated with the change in the bond angles of the groups attached to the phosphorus atom. In order to explain the linear correlation between the cone angle and the coordination shift for  $\text{RhCl}(\text{CO})\text{L}_2$ , Tolman [11] indicated that ligands having smaller cone angles tend to open the CPC or OPO angles of the ligand wider during coordination. In the present case, although the phosphorus ligands having similar cone angles were used, different coordination shifts were observed. Furthermore, the coordination shifts decrease with an increase in  $\chi$ . These facts indicate that the variation in the coordination shift is mainly caused by the electronic change accompanied by the coordination. Therefore, the coordination shift would be a measure of the net electron drift between the rhenium(I) and the phosphorus atom in the complexes.

Table 5  
 XPS data for  $[\text{Re}(\text{bpy})(\text{CO})_3\text{L}][\text{SbF}_6]^\text{a}$

No.	L	Binding energy (eV)		
		$\text{Re}(4f_{7/2})$	$\text{P}(2p)$	$\text{N}(1s)$
1	$\text{P}(\text{n-Bu})_3$	42.0	131.1	400.7
2	$\text{PEt}_3$	41.8	131.2	400.8
3	$\text{PPh}_3$	42.0	131.4	400.6
4	$\text{P}(\text{OMe})\text{Ph}_2$	41.7	132.0	400.4
5	$\text{P}(\text{O}^i\text{Pr})_3$	41.8	133.1	400.4
6	$\text{P}(\text{OEt})_3$	41.7	133.3	400.5
7	$\text{P}(\text{OMe})_3$	41.8	133.2	400.4
8	$\text{P}(\text{OPh})_3$	41.9	133.6	400.7

<sup>a</sup> The binding energy was referred to  $\text{F}(1s)$  peak (686.0 eV). The error of the binding energy determination was estimated to be  $\pm 0.1$  eV.

### 3.7. X-ray photoelectron spectra

Table 5 summarizes the XPS data. Although there have been several reports on XPS of transition metal complexes having phosphorus ligands [21,25–29], only one report has focused on the changes in the binding energy of the metal after the substitution of phosphorus ligands similar to the present case: that was a series of  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{L}]$  (L = phosphine, phosphite) [25]. In that series, the  $\text{Fe}(2p_{3/2})$  and  $\text{Fe}(3p)$  binding energy systematically varied with the electron-acceptor strength of ligand L. However, in the present case, the changes induced by a variation in ligand L are too small to have any influence on the  $\text{Re}(4f_{7/2})$  binding energy.

In contrast, the  $\text{P}(2p)$  binding energy increases with an increase in  $\chi$ . This indicates that the alkyl or alkoxy group directly attached to the phosphorus atom strongly affects the electron density of the phosphorus atom. The stronger the electron withdrawing of the group directly attached to the phosphorus atom, the greater the decrease of the electron density on the phosphorus atom. Therefore,  $\text{P}(2p)$  binding energy increases with an increase in  $\chi$ .

## 4. Conclusions

The rhenium complexes  $[\text{fac-Re}(\text{bpy})(\text{CO})_3\text{L}][\text{SbF}_6]$  (L = phosphine, phosphite) have been prepared and characterized by the IR, UV-vis,  $^1\text{H}$  NMR,  $^{31}\text{P}$  NMR, XPS and electrochemical techniques. Variations in the electronic properties related to the carbonyl ligands, rhenium(I), and L, i.e. CO stretching, MLCT transition, oxidation potential of the rhenium(I), and  $^{31}\text{P}$  NMR chemical shifts, were interpreted on the basis of the electron-acceptor strength of L. In contrast, the properties related to the bpy ligand, e.g. the redox potential corresponding to  $[\text{Re}(\text{bpy})(\text{CO})_3\text{L}]^+ / [\text{Re}(\text{bpy}^-)(\text{CO})_3\text{L}]$ , showed complicated changes after the substitution of L, indicating that other factors should be taken into account, in addition to the electron-acceptor strength of L. It is clear from these data that the systematic variation in ligand L is suitable for varying the electronic properties of the rhenium(I), carbonyl, and L ligands, which may in turn have an influence regarding their  $\text{CO}_2$  reduction properties. Studies on the  $\text{CO}_2$  reduction properties of these complexes are being carried out in our laboratory.

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