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## Preparation and Characterization of the Paramagnetic Rhenium Complex, $(\text{CO})_4\text{ReL}_2[\text{L}_2 = 2,3\text{-Bis}(\text{diphenylphosphino})\text{maleic anhydride}]$

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The paramagnetic complex of  $(\text{CO})_4\text{ReL}_2[\text{L}_2 = 2,3\text{-Bis}(\text{diphenylphosphino})\text{maleic anhydride}]$  was prepared both by the photochemically induced homolytic splitting of  $\text{Re}_2(\text{CO})_{10}$  with  $\text{L}_2$  and by the chemical reduction of  $[(\text{CO})_4\text{ReL}_2]\text{SO}_3\text{CF}_3$ . The  $(\text{CO})_4\text{ReL}_2$  compound was characterized by ESR spectrum. The spectrum exhibits three group of sextets arising from one  $^{185,187}\text{Re}$  nucleus ( $I=5/2$ ) and two equivalent  $^{31}\text{P}$  nuclei ( $I=1/2$ ). Infrared, ESR, and cyclic voltammetric data are reported for all of the complexes prepared in this study.

### Introduction

Paramagnetic 19-electron complexes play a vital role in the organometallic chemistry because many reactions have been found in which these complexes are involved as intermediates whenever metal radicals are formed<sup>1</sup>. The isolation and characterization of the paramagnetic complexes are relatively rare due to the instability of transient species<sup>2</sup>. However, ligands with low-energy, conjugated  $\pi^*$  orbitals such as quinones<sup>3</sup>,  $\alpha$ -diimines<sup>4</sup>, nitrosyls<sup>5</sup>, substituted pyridines<sup>6</sup>, and 2,3-bis(diphenylphosphino)maleic anhydride<sup>7</sup> are capable of stabilizing 19-electron organometallic complexes. The relative stability of the complexes can be attributed to the ability

of the ligands to delocalize the extra electron. Therefore, the term "18+ $\delta$  complex" is used to describe 19-electron organometallic complexes which are essentially 18-electron complexes with reduced ligands<sup>8</sup>.

Recently, Fenske<sup>7b</sup> reported the 19-electron complexes,  $\text{Co}(\text{CO})_3\text{L}_2$  and  $\text{Mn}(\text{CO})_4\text{L}_2$  [ $\text{L}_2 = 2,3\text{-Bis}(\text{diphenylphosphino})\text{maleic anhydride}$ ], by the reaction of  $\text{Co}_2(\text{CO})_8$  and  $\text{Mn}_2(\text{CO})_{10}$  with  $\text{L}_2$ , respectively. The 19-electron complexes showed that the unpaired electron is delocalized over the transition metal atom and the  $\pi^*$  system of the  $\text{L}_2$  ligand. The ease of the formation of complexes,  $\text{Co}(\text{CO})_3\text{L}_2$  and  $\text{Mn}(\text{CO})_4\text{L}_2$ , by chemical reaction prompted us to study the 19-electron complex,  $\text{Re}(\text{CO})_4\text{L}_2$ . However, the reaction of  $\text{Re}_2(\text{CO})_{10}$  and  $\text{L}_2$  even

under the forcing reaction condition did not result in the formation of the desired complex,  $\text{Re}(\text{CO})_4\text{L}_2$ . Therefore alternative pathways have been taken for the formation of the complex,  $\text{Re}(\text{CO})_4\text{L}_2$ . One method is to generate the 19-electron species by photochemical reaction reported by us<sup>9</sup>. The other method is to synthesize the diamagnetic complex,  $[(\text{CO})_4\text{ReL}_2]\text{SO}_3\text{CF}_3$ , and to reduce this complex with the use of cobaltocene.

In this paper, we wish to report the preparation, characterization and reaction of the paramagnetic rhenium complex.

## Experimental Section

**General.** All manipulation of air-sensitive materials were carried out under an argon atmosphere with the use of standard Schlenk, vacuum line technique or a Mebraun MB150 glovebox system. Reagent grade benzene, hexane, toluene, and tetrahydrofuran (THF) were distilled under argon from sodium-benzophenone ketyl. Dichloromethane was distilled under argon from calcium hydride.  $^1\text{H}$ -NMR and  $^{31}\text{P}$ -NMR spectra were recorded on a Bruker WM-250 spectrometer in  $\text{CD}_3\text{CN}$ . Chemical shifts were given in parts per million relative to tetramethylsilane for  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra, 85%  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}$ -NMR spectra. Cyclic voltammetry was carried out using a EG & G Potentiostat/Galvanostat Model 273 with a glassy-carbon working electrode and an Ag/AgCl reference electrode and tetra-*n*-butyl-ammonium perchlorate (TBAP) as an electrolyte in  $\text{CD}_3\text{CN}$ . IR spectra were obtained by using a Perkin-Elmer 1310 instrument. Conductivity measurement was conducted with an Industrial Instrument Model RC216B2. Elemental analyses were carried out at the Basic Science Research Center. The  $\text{Re}(\text{CO})_5\text{Br}$ <sup>10</sup>,  $\text{Re}(\text{CO})_5\text{OSO}_2\text{CF}_3$ <sup>11</sup>,  $\text{Ph}_2\text{PNa}$ <sup>12</sup>,  $(\text{CH}_3)_3\text{SiPPh}_2$ <sup>12</sup>, and 2,3-Bis(diphenylphosphino)maleic anhydride<sup>7c</sup> were prepared according to the literature methods. Rhenium decacarbonyl, Diphenylchlorophosphine, Trimethylchlorosilane, 1,2-Bis(diphenylphosphino)ethylene, Bis(cyclopentadienyl)cobalt(II), and  $\text{MCl}_3 \cdot x\text{H}_2\text{O}$  ( $\text{M} = \text{Rh}, \text{Ir}$ ) were purchased from Strem Chemicals.

**Preparation of  $[(\text{CO})_4\text{ReL}_2]\text{SO}_3\text{CF}_3$  [ $\text{L}_2 = 2,3$ -bis(diphenylphosphino)maleic anhydride](I).** To a stirred dichloromethane (15 ml) solution of  $\text{Re}(\text{CO})_5\text{Br}$  (0.14 g, 0.36 mmol) was added  $\text{AgSO}_3\text{CF}_3$  (0.1 g, 0.40 mmol). The solution was stirred at room temperature for additional 2 h. The solution was filtered in order to remove AgCl and evaporated to dryness. To this complex was combined 2,3-bis(diphenylphosphino)maleic anhydride (0.16 g, 0.36 mmol) and charged toluene (20 ml). The red solution was refluxed for 4 h. After the solution was cooled to room temperature, the volume was reduced to ca. 5 ml. The red precipitate was filtered and recrystallized from dichloromethane/hexane to give I in 17% yield. mp. 208°C.  $\Lambda = 76.8 \Omega^{-1}\text{mol}^{-1}\text{cm}^2$ .  $^{31}\text{P}$ -NMR (121.50 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ 20.93. IR( $\text{CH}_3\text{CN}$ )  $\nu(\text{C}\equiv\text{O})$  2061, 2019, 2008, 1991,  $\nu(\text{C}=\text{O})$  1778, 1712  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{33}\text{F}_3\text{H}_{20}\text{O}_{10}\text{P}_2\text{ReS}$ : C, 43.36; H, 2.19; S, 3.51. Found: C, 43.18; H, 1.89; S, 3.83.

**Preparation of  $[(\text{CO})_4(\text{dppe})\text{Re}]\text{SO}_3\text{CF}_3$  [ $\text{dppe} = 1,2$ -bis(diphenylphosphino)ethylene](II).** To a stirred dichloromethane (20 ml) solution of  $\text{Re}(\text{CO})_5\text{Br}$  (0.25 g, 0.62 mmol) was added  $\text{AgSO}_3\text{CF}_3$  (0.24 g, 0.93 mmol). The solution was stirred for 2 h and filtered. To the filtrate was added

1,2-bis(diphenylphosphino)ethylene (0.44 g, 1.12 mmol) dissolved in a minimum amount of dichloromethane. The solution was stirred for 14 h and concentrated to ca. 6 ml under the reduced pressure and hexane (5 ml) was added to the solution. On cooling the solution, the white precipitate was formed and this crystalline material was filtered and washed with hexane ( $2 \times 5$  ml). Yield: 37%. mp. 195°C.  $\Lambda = 73.4 \Omega^{-1}\text{mol}^{-1}\text{cm}^2$ .  $^{31}\text{P}$ -NMR (121.50 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ -28.19.  $^1\text{H}$ -NMR  $\delta$  7.95-6.92(m, 20H), 2.17(m, 2H). IR( $\text{CH}_3\text{CN}$ )  $\nu(\text{C}\equiv\text{O})$  2050, 2037, 1985, 1930  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{31}\text{F}_3\text{H}_{22}\text{O}_7\text{P}_2\text{ReS}$ : C, 44.10; H, 2.61; S, 3.80. Found: C, 44.31; H, 2.55; S, 3.81.

**Preparation of  $\text{Re}(\text{CO})_3\text{L}_2\text{Br}$  [ $\text{L}_2 = 2,3$ -bis(diphenylphosphino)maleic anhydride](III).** To a stirred solution of 0.125 mmol of  $\text{Re}(\text{CO})_5\text{Br}$  in 5 ml of THF was slowly added a solution of 0.127 mmol of 2,3-bis(diphenylphosphino)maleic anhydride in THF (5 ml). The solution was refluxed for 3 h and evaporated to dryness. The red product was recrystallized from dichloromethane/hexane and dried in vacuo. Yield: 22%. mp. 183°C. IR (THF)  $\nu(\text{C}\equiv\text{O})$  2019, 1965, 1914,  $\nu(\text{C}=\text{O})$  1773, 1717  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{31}\text{H}_{20}\text{O}_6\text{P}_2\text{ReBr}$ : C, 45.60; H, 2.47. Found: C, 46.27; H, 2.52.

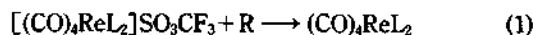
**Preparation of  $\text{Re}(\text{CO})_4\text{L}_2$  [ $\text{L}_2 = 2,3$ -bis(diphenylphosphino)maleic anhydride](IV).** To a stirred tetrahydrofuran (5 ml) solution of  $[(\text{CO})_4\text{ReL}_2]\text{SO}_3\text{CF}_3$  (0.18 g, 0.2 mmol) was added a THF (5 ml) solution of 0.8 mmol of bis(cyclopentadienyl) cobalt. The reaction mixture was stirred for 4 h. After the reaction was completed (as monitored by IR spectroscopy), hexane (3 ml) was added. The orange product was filtered and recrystallized from dichloromethane and hexane. Yield: 38%. mp. 168-176°C(dec.). IR(THF)  $\nu(\text{C}\equiv\text{O})$  2061, 2012, 1958, 1930  $\nu(\text{C}=\text{O})$  1672, 1624  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{21}\text{H}_{20}\text{O}_7\text{P}_2\text{Re}$ : C, 50.26; H, 2.64. Found: C, 49.84; H, 2.36.

**Preparation of  $\text{Re}(\text{CO})_4\text{L}_2\text{I}$  [ $\text{L}_2 = 2,3$ -bis(diphenylphosphino)maleic anhydride](V).** To a stirred THF (5 ml) solution of  $[(\text{CO})_4\text{ReL}_2]$  (0.15 g, 0.168 mmol) was added iodine (0.075 g). Upon addition of iodine, red product was precipitated out. The solution was stirred at room temperature for additional 1 h. The red precipitate was filtered and washed with hexane ( $2 \times 5$  ml). Yield: 84%. mp. 217-222°C(dec.). IR(THF)  $\nu(\text{C}\equiv\text{O})$  2075, 2025, 2010, 1987  $\nu(\text{C}=\text{O})$  1782, 1710  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{32}\text{H}_{20}\text{O}_7\text{P}_2\text{ReI}$ : C, 43.11; H, 2.24. Found: C, 42.48; H, 2.11.

## Results and Discussion

### Preparation of $(\text{CO})_4\text{ReL}_2$ Complex

**Chemical Method.** The paramagnetic rhenium complex has been prepared according to Eq. (1).



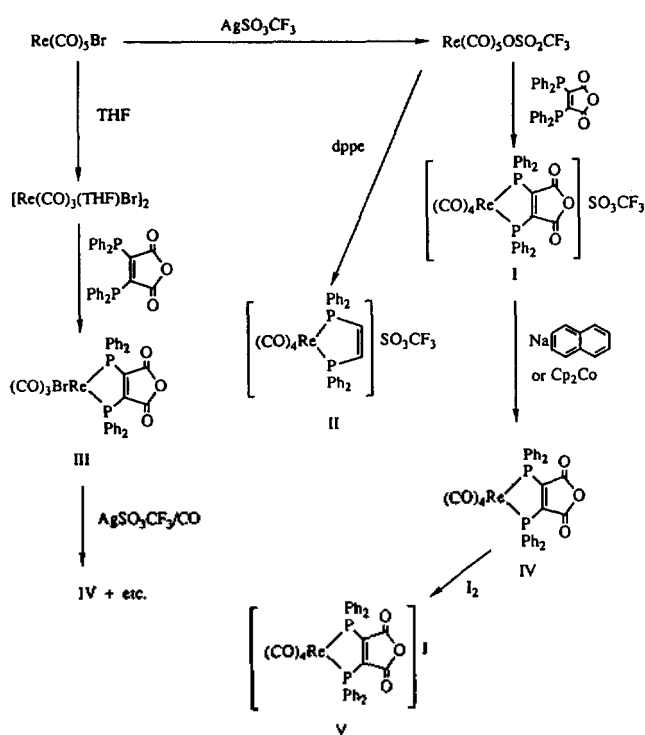
$\text{L}_2 = 2,3$ -bis(diphenylphosphino)maleic anhydride  
 $\text{R} =$  sodium naphthalenide and cobaltocene

The addition of cobaltocene to a stirred THF solution of  $[(\text{CO})_4\text{ReL}_2]\text{SO}_3\text{CF}_3$  gave an orange solution. The addition of hexane to the solution affords an orange precipitate. The resulting orange complex,  $(\text{CO})_4\text{ReL}_2$  was isolated as an air-sensitive solid in relatively good yield. The diamagnetic rhenium complex  $[(\text{CO})_4\text{ReL}_2]\text{SO}_3\text{CF}_3$ (I) was prepared from the reaction of  $\text{Re}(\text{CO})_5\text{SO}_3\text{CF}_3$  and  $\text{L}_2$  in toluene under the re-

**Table 1.** Infrared Spectroscopic Data

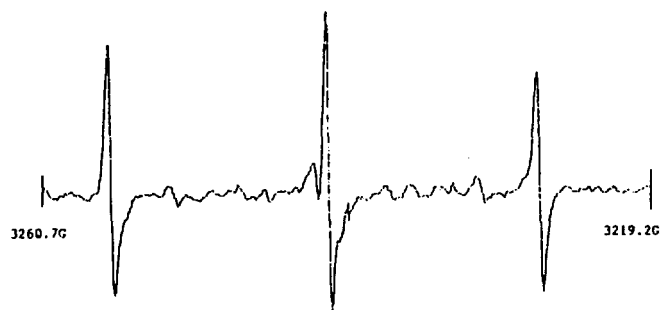
Complex	$\nu(\text{CO}), \text{cm}^{-1}$	$\nu(\text{C}=\text{O}), \text{cm}^{-1}$	Medium	Reference
$(\text{CO})_5\text{MnL}_2^a$	2082, 2018, 1998, 1971	1662, 1621, 1609	KBr	7(b)
$[(\text{CO})_4\text{ReL}_2]\text{SO}_3\text{CF}_3^b$	2061, 2019, 2008, 1991	1778, 1712	$\text{CH}_3\text{CN}$	this work
$(\text{CO})_4\text{ReL}_2^b$	2061, 2012, 1958, 1930	1672, 1624	THF	this work
$[(\text{CO})_4\text{ReL}_2]^b$	2075, 2025, 2010, 1987	1782, 1710	THF	this work

<sup>a</sup>  $\text{L}_2 = 2,3\text{-bis}(\text{diphenylphosphino})\text{-N-methylmaleic anhydride}$ . <sup>b</sup>  $\text{L}_2 = 2,3\text{-bis}(\text{diphenylphosphino})\text{maleic anhydride}$ .

**Scheme 1.**

fluxing reaction condition (see Scheme 1). Initially, we attempted the reaction of  $\text{Re}(\text{CO})_5\text{Br}$  and  $\text{L}_2$  under the refluxing condition. However, the reaction did not lead to formation of the complex  $[(\text{CO})_4\text{ReL}_2]\text{Br}$ . Therefore, we thought that the reaction of  $\text{Re}(\text{CO})_5\text{SO}_3\text{CF}_3$  and  $\text{L}_2$  would proceed to give the complex  $[(\text{CO})_4\text{ReL}_2]\text{SO}_3\text{CF}_3$  (I) if a relatively strong Re-Br bond was converted into a weak Re-O bond. It is also interesting to note that the complex  $[\text{Re}(\text{bpm})(\text{CO})_4]\text{SO}_3\text{CF}_3$  (bpm = 2,2'-bipyrimidine) was prepared by the reaction of  $\text{Re}(\text{CO})_5\text{SO}_3\text{CF}_3$  and bpm<sup>11</sup>. As a second approach to the preparation of  $[(\text{CO})_4\text{ReL}_2]\text{SO}_3\text{CF}_3$ , we carried out the reaction of the  $[\text{Re}(\text{CO})_3(\text{THF})\text{Br}]_2$  complex and  $\text{L}_2$  to give  $(\text{CO})_3\text{BrReL}_2$  (V). The preparation of  $[(\text{CO})_4\text{ReL}_2]\text{SO}_3\text{CF}_3$  may be envisioned by the introduction of one CO to and removal of Br from the complex V. Therefore, carbon monoxide (1 atm) was introduced to a THF solution of the complex V in the presence of  $\text{AgSO}_3\text{CF}_3$ . However, the reaction gave the complex I in less pure form.

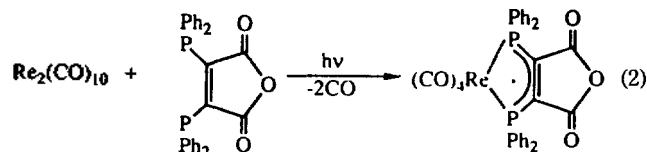
The structures of the compounds I, IV and V were deduced by spectroscopic methods. The infrared spectrum of I (see Table 1) displays four absorption bands as 2061, 2019, 2008, and 1991  $\text{cm}^{-1}$  in the carbonyl region, as expected from  $\text{C}_{2v}$  symmetry group ( $2\text{A}_1 + \text{B}_1 + \text{B}_2$ ). The IR spectrum



**Figure 1.** The ESR spectrum of the THF solution containing  $\text{Re}_2(\text{CO})_{10}$  and 2,3-bis(diphenyl phosphino)maleic anhydride in the dark at room temperature.

of IV also shows four absorption bands at 2061, 2012, 1958, and 1930  $\text{cm}^{-1}$  in the carbonyl region. The lower frequency shift of CO stretching in IV is attributable to the back bonding due to the excess electron density in the  $(\text{CO})_4\text{ReL}_2$  complex. The IR spectrum of the complex V shows three absorption bands at 2050, 1985, and 1930  $\text{cm}^{-1}$ . The values are very close to those of the known complex,  $\text{Re}(\text{CO})_3\text{Br}[\text{P}(\text{OPh})_3]_2$ <sup>13</sup>. The <sup>31</sup>P-NMR spectrum of I exhibits one singlet at  $\delta$  20.93, indicating that two phosphorus atoms are chemically equivalent.

**Photochemical Method.** The photochemically induced disproportionation reactions of metal-metal bonded dimer are well documented<sup>14</sup>. Recently, Wan and coworker<sup>15</sup> reported that an organometallic radical complex, the rhenium carbonyl-3,5-di-tert-butyl-*o*-quinone complex was readily formed during the photolysis of benzene solution containing both the parent quinone and  $\text{Re}_2(\text{CO})_{10}$ . The ease of the formation of transient  $\text{Re}(\text{CO})_5$  radical from the dimer  $\text{Re}_2(\text{CO})_{10}$  by photochemical method<sup>15</sup> prompted us to study the 19-electron species  $(\text{CO})_4\text{ReL}_2$ .



The ESR spectrum of a THF solution of  $\text{Re}_2(\text{CO})_{10}$  (10 mmol) and  $\text{L}_2$  [2,3-bis(diphenylphosphino)maleic anhydride] (10 mmol) in the dark at room temperature is shown in Figure 1. The radical, which is stable, exhibits the 1:2:1 triplets arising from the equivalent <sup>31</sup>P nuclei. The coupling constant of the reduced ligand ( $a_p = 8.92$  G) indicates that the unpaired electron density is polarized toward the phosphorus atoms. The large value of  $a_p$  is in contrast with that of the reduced form in  $\text{L}_2$  ( $a_p = 3.10$  G), which indicates tha

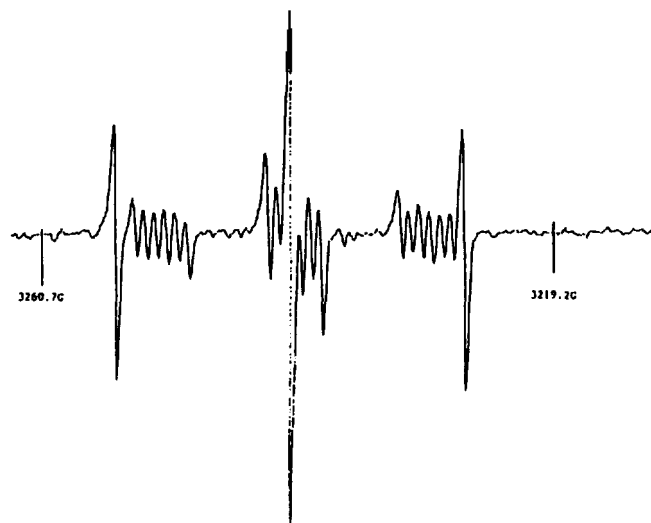


Figure 2. The ESR spectrum after the irradiation of the solution for 2 min.

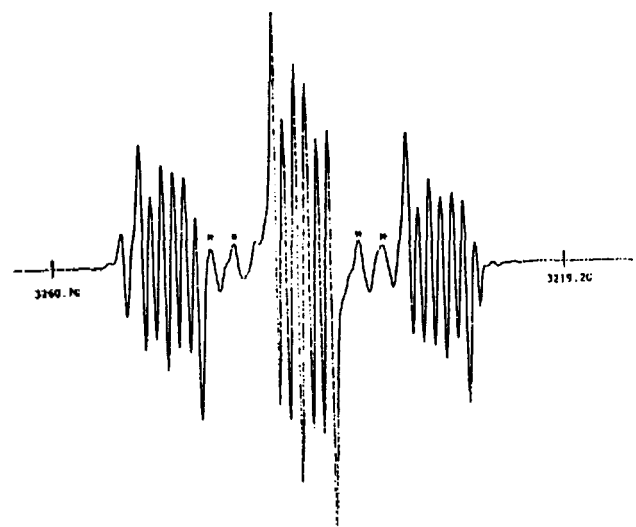


Figure 3. The ESR spectrum after the irradiation of the solution for 15 min. The asterisk are due to the impurity.

the unpaired electron is polarized toward the oxygen atoms. The  $g$  value ( $g=2.0036$ ) is close to the free electron value ( $g_e=2.0023$ ) and those for  $\text{Re}(\text{CO})_3\text{L}_2$  ( $\text{L}=i\text{-Pr-DAB}$ ,  $t\text{-Bu-DAB}$ ,  $p\text{-tol-DAB}$ ) radical complexes reported by Stufkens and coworkers<sup>16</sup>.

The progress of irradiation without cutoff filter results in a homolytic splitting of the metal-metal bond, leading to the formation of radical species,  $\text{Re}(\text{CO})_3\text{L}_2$ . Upon irradiation, the color of the solution was changed from yellow orange due to the formation of the radical species. The ESR spectra of  $\text{Re}(\text{CO})_3\text{L}_2$  in THF at room temperature after the irradiation of the solution for 2 and 15 min are shown in Figure 2 and 3, respectively. The photochemical reaction was monitored by IR. The formation of radical complex was completed within 20 min. Best-fit simulated ESR spectrum (see Figure 4) was obtained for the  $\text{Re}(\text{CO})_3\text{L}_2$  radical by direct comparison of the experimental spectrum with line shapes calculated for a wide variety of hyperfine parameters. The infrared spec-

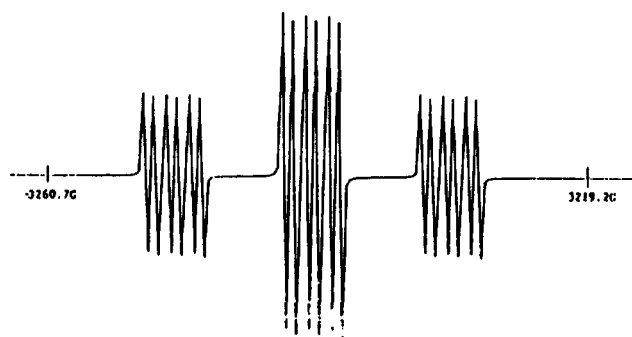


Figure 4. Best-fit simulated ESR spectrum.

Table 2. ESR Data

Complex	$a_p$	$a_m$	$g$	Reference
$\text{L}_2^-$	3.10		2.0077	7(c)
$(\text{CO})_3\text{CoL}_2$	9.72	1.05	2.0041	7(c)
$(\text{CO})_3\text{MnL}_2$	10.25			7(b)
$(\text{CO})_3\text{ReL}_2$	10.60	0.89	2.0048	this work

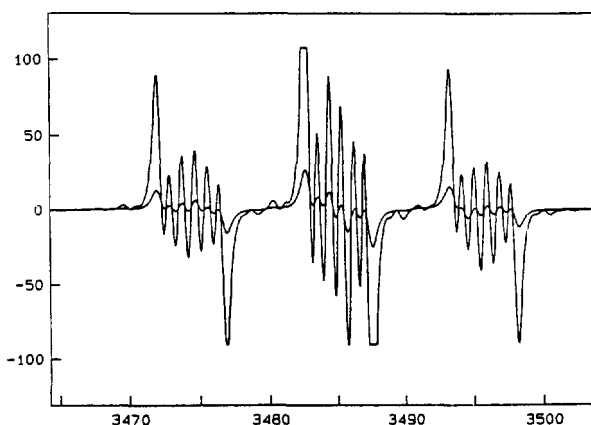
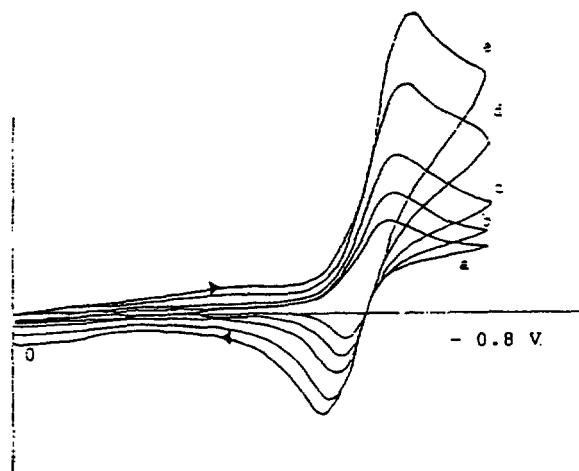


Figure 5. X-band ESR spectrum of  $(\text{CO})_4\text{ReL}_2$  in THF at 25°C. Strong line; reduced by sodium naphthalenide, Weak line; reduced by cobaltocene.

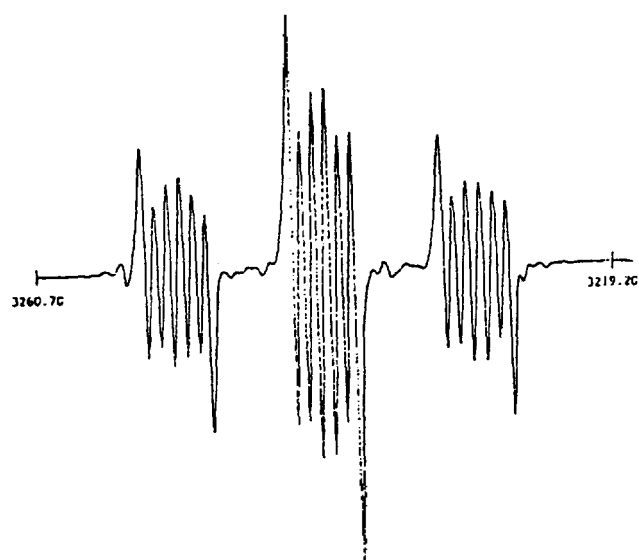
trum of the radical complex in THF shows four absorption bands in the carbonyl region. Evaporation of the solution gives an orange paramagnetic powder.

#### ESR Spectrum of $(\text{CO})_4\text{ReL}_2$

The coupling constants and  $g$  value in the ESR spectrum of the  $(\text{CO})_4\text{ReL}_2$  complex are summarized in Table 2. The X-band ESR spectrum of  $(\text{CO})_4\text{ReL}_2$  in THF at 25°C is shown in Figure 5. The spectrum exhibits three groups of sextets arising from one  $^{185,187}\text{Re}$  nucleus ( $I=5/2$ ) and two equivalent  $^{31}\text{P}$  ( $I=1/2$ ) nuclei. The large phosphorus coupling constant ( $a_p=10.60$  G) and small rhenium coupling constant ( $a_{Re}=0.89$  G) indicate the the unpaired electron has a greater interaction with the phosphorus atoms in the complexes due to the delocalization of the electron onto the  $\text{Re}(\text{CO})_4$  portion of the molecule. The  $g$  value ( $g=2.0048$ ) of radical complex is still close to that of the free electron. This means that the unpaired electrons resides at the ligand, and the radical



**Figure 6.** Ambient temperature cyclic voltammogram of  $1.02 \times 10^{-4}$  M  $[(\text{CO})_4\text{ReL}_2]\text{SO}_3\text{CF}_3$  in THF containing 0.12 M  $n\text{-Bu}_4\text{NClO}_4$  measured at a platinum electrode at a scan rate of a) 0.05, b) 0.1, c) 0.2, d) 0.5, e) 1.0  $\text{VS}^{-1}$ .



**Figure 7.** The ESR spectrum of a mixture of  $\text{Re}(\text{CO})_4\text{L}_2$  [ $\text{L}_2 = 2,3\text{-bis}(\text{diphenylphosphino})\text{maleic anhydride}$ ] and  $\text{P}(\text{OMe})_3$  at room temperature.

is essentially considered as the 18 electron anion complex in rhenium is surrounded by four carbonyl groups and a negatively charged diphosphine ligand.

#### Electrochemistry of $[(\text{CO})_4\text{ReL}_2]\text{SO}_3\text{CF}_3$ and $(\text{CO})_4\text{ReL}_2$

The relative stability of the  $(\text{CO})_4\text{ReL}_2$  complex can be attributed to the ability of the  $\text{L}_2$  ligand to delocalize the extra electron. The role of the ligand to accept an electron suggests that the complex would be electrochemically reversible. A cyclic voltammogram of  $[(\text{CO})_4\text{ReL}_2]\text{SO}_3\text{CF}_3$  in  $\text{CH}_2\text{Cl}_2$  is shown in Figure 6. Under the specified conditions, the compound exhibits a quasi-reversible one electron reduction of at  $E_{1/2} = -0.62$  V vs SCE. The peak potential changes slightly according to the scan rate ranging from 0.05 to 0.50  $\text{VS}^{-1}$ . In addition,  $i_p, a/i_p, c$  increases with increasing scan rate from 0.74 at 0.05  $\text{VS}^{-1}$  to 0.95 at 0.5  $\text{VS}^{-1}$  with  $\Delta E_p = 134$  and

268 mV, respectively. These data are indicative of chemical reversibility being associated with the following reduction process. From the following chemical reversibility in Eq. (3), it was assumed that the 19-electron  $[(\text{CO})_4\text{ReL}_2]$  radical could be prepared by the reducing reagents such as sodium naphthalenide or cobaltocene.



#### Reactivity of the $(\text{CO})_4\text{ReL}_2$ Complex

Since it has been known that the paramagnetic complex is substitutionally labile, we attempted to react the  $(\text{CO})_4\text{ReL}_2$  complex with phosphine ligands such as  $\text{P}(\text{OMe})_3$ ,  $\text{PPh}_3$ , and  $\text{PEt}_3$  in THF. Unexpectedly, the product was turned out to be a diamagnetic compound rather than one substituted phosphine product. The ESR spectrum, immediately taken from the addition of  $(\text{CO})_4\text{ReL}_2$  and  $\text{P}(\text{OMe})_3$  at room temperature is shown in Figure 7. The ESR spectrum taken after leaving the mixture for 1 hour was completely silent, indicating that the product is diamagnetic presumably due to the formation of a dimer. The reason why the radical complex is substitutionally unstable and decomposed to form a dimer may be attributable to the steric hindrance. The inertness of the rhenium complex is quite surprising on view of the easy substitution reactions of the  $(\text{CO})_3\text{CoL}_2$  with phosphines. Oxidation of the  $(\text{CO})_4\text{ReL}_2$  complex with an equivalent of  $\text{I}_2$  readily occurred. In a typical experiment, addition of  $\text{I}_2$  to a stirred THF solution of  $(\text{CO})_4\text{ReL}_2$  gave red precipitate. The red product was recrystallized from dichloromethane and hexane. The infrared spectrum of the  $[(\text{CO})_4\text{ReL}_2]$  I complex shows four absorption bands at 2075, 2025, 2010, and 1987  $\text{cm}^{-1}$  in the carbonyl region. The peaks were shifted to higher frequencies than those of the  $(\text{CO})_4\text{ReL}_2$  complex. The values are in good agreement with those of the  $[(\text{CO})_2\text{ReL}_2]\text{SO}_3\text{CF}_3$  complex.

#### Concluding Remarks

The paramagnetic complex of  $(\text{CO})_4\text{ReL}_2$  can be obtained via a homolytic splitting of the metal-metal bonded complex,  $\text{Re}_2(\text{CO})_{10}$ . The  $(\text{CO})_4\text{ReL}_2$  complex can be also prepared from the chemical reduction of  $[(\text{CO})_4\text{ReL}_2]\text{SO}_3\text{CF}_3$ . The unpaired electron essentially resides on the ligand as indicated by the ESR spectrum. The radical complex is substitutionally unstable and decomposed to form a dimer due to the steric hindrance of ligand.

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## Effect of SDS on Retention of Nucleic Acid Components in High-Performance Liquid Chromatography

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The effect of the addition of sodium dodecyl sulfate (SDS) to a buffered mobile phase (pH 3.4) on the retention of nucleotides, nucleosides and bases was investigated with a polyvinyl alcohol (PVA) column. Depending on the concentration of SDS, two different trends in the retention of nucleosides and bases containing an NH<sub>2</sub> group were observed. If the concentration of SDS was less than 5.5 mM, the retention of compounds containing an NH<sub>2</sub> group increased as the concentration of SDS in the mobile phase increased. In contrast, if the concentration was greater than 5.5 mM, the retention of compounds containing an NH<sub>2</sub> group decreased. Thus, the SDS acted as an ion-pairing reagent at lower concentration but formed micelles at higher concentrations. The retention behavior of the nucleosides and bases in the presence of a micellar concentration of SDS in the mobile phase on the PVA column was compared to the retention behavior on other types of columns.

### Introduction

During the past decade, high-performance liquid chromatography (HPLC) has been extensively used for the separation of nucleotides, nucleosides and bases<sup>1-14</sup>. These HPLC methods include ion exchange<sup>1-4</sup>, reversed-phase<sup>5-10</sup> and ion pair<sup>11-14</sup> liquid chromatography. Among these methods, the effects of small amount of surfactants in the mobile phase have been investigated in ion pair chromatography<sup>15-21</sup>. Kraak *et al.*<sup>20</sup> investigated the retention behavior of nucleosides and bases on a reversed-phase C<sub>18</sub> column using water-ethanol solutions containing small amount of SDS as the mobile phase. In 1980, Armstrong and Henry reported the use of an aqueous micellar solution as a selective mobile phase in reversed-phase liquid chromatography<sup>22</sup>. Since then, micellar liquid chromatography has been investigated for the

separation of many types of compounds<sup>23-32</sup>.

Most of the separations of nucleic acid components reported have been performed on silica-based columns. Recently, the retention behavior of nucleotides, nucleosides and their bases on a polymeric polyvinyl alcohol (PVA) column with several different buffer and salt solutions have been reported<sup>33-37</sup>. However, detailed information on the characteristics of PVA columns is not available.

We previously reported the use of micellar mobile phases for the separation of nucleosides and bases on a column<sup>29</sup>. Effect of pH, temperature, and concentration of SDS and the counter ion on retention behavior were investigated. In this paper, we extended the studies on the retention behavior of nucleotides, nucleosides and bases on a PVA column using SDS mobile phases. Effect of different stationary phases on the separation of nucleosides and bases was also