

# Electronic Emission and Absorption Spectroscopy of the Rhenium Complexes $\text{Re}(\text{CO})_3\text{Cl}(\text{Phosphine})_2$

M. N. Ramsis

Chemistry Department, Faculty of Science, Ain Shams University, Abbassia, Cairo, Egypt

**Summary.** The compounds  $\text{Re}(\text{CO})_3\text{Cl}(L)_2$ ,  $L$  = triphenylphosphine, tri-*p*-tolylphosphine, and  $\text{Re}(\text{CO})_3\text{Cl}(L)$ ,  $L$  = 1,2-bis(diethylphosphinoethane) are luminescent in solution and in crystalline form when excited between 351 nm and 514 nm at temperatures ranging from 10 K to room temperature. The absorption spectra contain a weak ( $E \sim 10 \text{ M}^{-1} \text{ cm}^{-1}$ ) band in the visible region of the spectrum between 400 and 500 nm. The lowest energy transition giving rise to these spectroscopic features is assigned to a d-d transition.

**Keywords.** Rhenium complexes; Electronic emission; Absorption.

## Elektronenemissions- und Absorptionsspektroskopie der Rheniumkomplexe $\text{Re}(\text{CO})_3\text{Cl}(\text{Phoshin})_2$

**Zusammenfassung.** Die Verbindungen  $\text{Re}(\text{CO})_3\text{Cl}(L)_2$  mit  $L$  = Triphenylphosphin, Tri-*p*-tolylphosphin und  $\text{Re}(\text{CO})_3\text{Cl}(L)$  mit  $L$  = 1,2-Bis(diethylphosphinoethan) sind in Lösung und im kristallinen Zustand bei Anregung zwischen 351 und 514 nm im Temperaturbereich von 10 K bis Raumtemperatur lumineszent. Die Absorptionsspektren enthalten im sichtbaren Bereich zwischen 400 und 500 nm eine schwache Bande von  $\epsilon \sim 10 \text{ M}^{-1} \text{ cm}^{-1}$ . Der energetisch tiefstliegende Übergang, der für dieses Verhalten verantwortlich ist, wird einem d-d-Übergang zugeordnet.

## Introduction

Luminescence of  $\text{Re}(\text{CO})_3\text{Cl}(L)$  where  $L$  is a bidentate  $\alpha$ -diimine ligand or two substituted pyridine ligands continues to attract interest [1–11]. The parent compound of the series,  $\text{Re}(\text{CO})_5\text{Cl}$ , is luminescent from a d-d excited state [12]. Substitution of two of the carbonyl ligands changes the lowest excited electronic state to a metal to ligand charge transfer state (MLCT) when  $L$  = bipyridine or *o*-phenanthroline, for example. The latter two complexes have been the most extensively studied because they exhibit unusual luminescence properties. Of most interest has been the observation of room temperature luminescence in fluid solution [8] and luminescence rigidochromism, the change in color depending on environmental rigidity [2].

As part of our interest in the use of luminescent probes of the local environment of organometallic molecules [11], we investigated the luminescence properties of phosphine derivatives of the type  $\text{Re}(\text{CO})_3\text{Cl}(L)_2$ ,  $L =$  triphenylphosphine, tri-*p*-tolylphosphine, and  $\text{Re}(\text{CO})_3\text{Cl}(L)$ ,  $L =$  1,2-bis(diethylphosphinoethane). These complexes contain phosphine ligands which are strong ligands in the spectrochemical series [13, 14] but which are not expected to have low lying  $\pi$  antibonding orbitals which could participate in MLCT transitions. We report here the results of luminescence spectroscopic studies of these complexes at room temperature and low temperature and compare the effects of the environment on the emission maxima with those on the known rigidochromic molecules.

## Experimental Part

The complexes  $\text{Re}(\text{CO})_3\text{Cl}(L)_2$  where  $L =$  triphenylphosphine (Aldrich Chemical Co.) and tri-*p*-tolylphosphine (Eastman) were prepared according to the reference procedure [15]. Pentacarbonylchlororhenium (Atomergic Chemical Corp.) and a five equivalent excess of ligand were heated at  $120^\circ$  in nitrogen until the evolution of CO ceased (ca. 30 min). After cooling, excess ligand was removed by washing with diethyl ether ( $3 \times 5$  ml) (Fisher Scientific). The residual solid was extracted in cold chloroform ( $2 \times 2$  ml). Light petroleum (15 ml) (Fisher Scientific) was added to the filtered solution and the solution was allowed to crystallize overnight. The crystals were washed with light petroleum ( $2 \times 2$  ml). Excess solvent was removed by using a rotary evaporator ( $20^\circ/0.1$  mm). The same procedure was used to prepare  $\text{Re}(\text{CO})_3\text{Cl}(L)$  where  $L =$  1,2-bis(diethylphosphinoethane) (Alfa products). The evolution of CO begins at about  $100^\circ$  and the total time of heating was 20 min. Recrystallization from ether, chloroform and light petroleum was necessary to obtain the pure product. Satisfactory elemental analyses (Desert Analytics) were obtained for the three complexes. All of the complexes exhibit the characteristic three band infrared spectrum in the CO existing region:  $L =$  triphenylphosphine, 2035, 1952, 1905;  $L =$  tri-*p*-tolylphosphine, 2034, 1969, 1899;  $L =$  1,2-bis(diethylphosphinoethane) 2027, 1951,  $1887 \text{ cm}^{-1}$ .

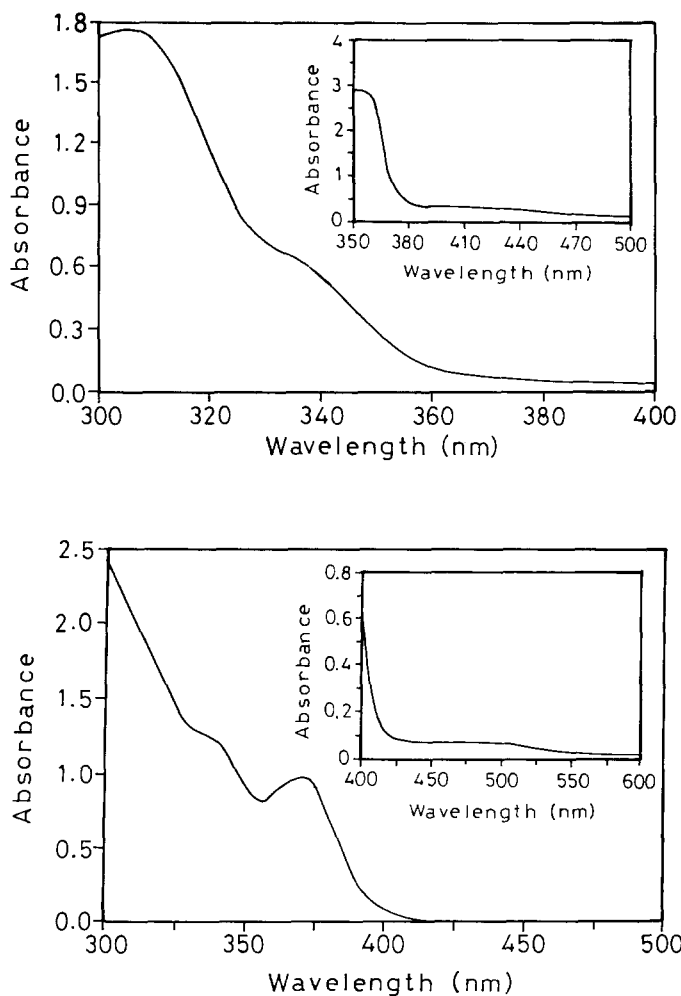
Infrared spectra were recorded from chloroform solutions using a Nicolet MX-1 spectrometer. UV-VIS absorption spectra between 200 and 600 nm were recorded from chloroform solutions using a HP-8651A Diode Array spectrophotometer.

Emission spectra were obtained by using an instrument described previously [16]. The sample temperature was controlled from between 298 K and 10 K using an Air Products displax closed cycle helium refrigerator. Spectra from crystals and frozen solutions ( $10^{-2} M$ ) were obtained. The excitation source was an Argon ion laser. The detector system consisted of a 3/4 meter SPEX 1702 single scanning monochromator, a C31034 photomultiplier tube, and a photon counter interfaced to an Apple computer.

## Results

### *Absorption Spectra*

The electronic absorption spectra of  $\text{Re}(\text{CO})_3\text{Cl}(\text{triphenylphosphine})_2$  and  $\text{Re}(\text{CO})_3\text{Cl}$ -1,2-bis(diethylphosphinoethane) are shown in Fig. 1. The positions of the maxima in the absorption spectra and the molar absorptivities of the compounds are given in Table 1. Two intense absorption regions are observed in the ultraviolet range between  $25\,000$  and  $33\,000 \text{ cm}^{-1}$  in the spectra of each of the compounds. Each of the complexes also exhibits a weak absorption peak in the visible region between  $20\,000$  and  $25\,000 \text{ cm}^{-1}$  ( $\epsilon = 4\text{--}18 M^{-1} \text{ cm}^{-1}$ ). This peak is slightly higher in energy



**Fig. 1.** The electronic absorption spectra of  $\text{Re}(\text{CO})_3\text{Cl}(\text{triphenylphosphine})_2$  (top) and  $\text{Re}(\text{CO})_3\text{Cl}$  1,2-bis(diethylphosphinoethane) (bottom) in chloroform at room temperature; the insets show enlargements of the visible region

**Table 1.** Electronic absorption maxima

Compound	Band maxima, nm			
	$(\epsilon, \text{M}^{-1} \text{cm}^{-1})$			
$\text{Re}(\text{CO})_3\text{Cl}(\text{triphenylphosphine})_2$	290 (2550)	340 (1280)	370 (1000)	490 (18)
$\text{Re}(\text{CO})_3\text{Cl}(\text{tri-}i>p\text{-tolylphosphine})_2$	295 (2560)	340 (800)	370 (500)	490 (6)
$\text{Re}(\text{CO})_3\text{Cl}$ 1,2-bis(diethylphosphinoethane)	300 (1700)	340 (800)		440 (3)

in the case of the complex containing the bidentate ligand 1,2-bis(diethylphosphinoethane) than are those in the spectra of complexes containing two monodentate phosphine ligands.

### Emission Spectra

All of the complexes are luminescent at 298 °K and 10 °K both in the solid state and in solution. The emission spectra are shown in Fig. 2 and the positions of the emission maxima are listed in Table 2.

The room temperature solution emission bands are structureless and less intense than those in the spectra of the crystals at the same temperature. The emission maxima in the solution spectra are modestly affected by changing the temperature from 298 °K to 10 °K, as shown in Fig. 3. This figure also shows the temperature dependence of the emission band of the rigidochromic complex.

In the case of  $\text{Re}(\text{CO})_3\text{Cl}(1,10\text{-phenanthroline})$  a sudden change in the wavelength of the emission maximum is observed between 195 °K and 175 °K. The intensity of the solution emission strongly increases as the temperature is decreased. The emission could be excited by using visible lines of the argon ion laser (457 nm, 488 nm and 514 nm) which are absorbed by the low energy transition in the absorption spectra ( $20\,000$  to  $25\,000\text{ cm}^{-1}$ ).

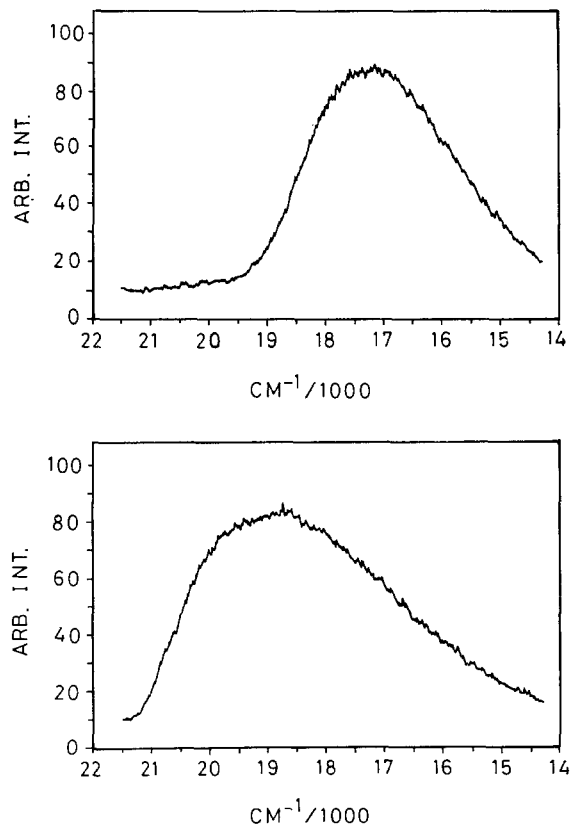


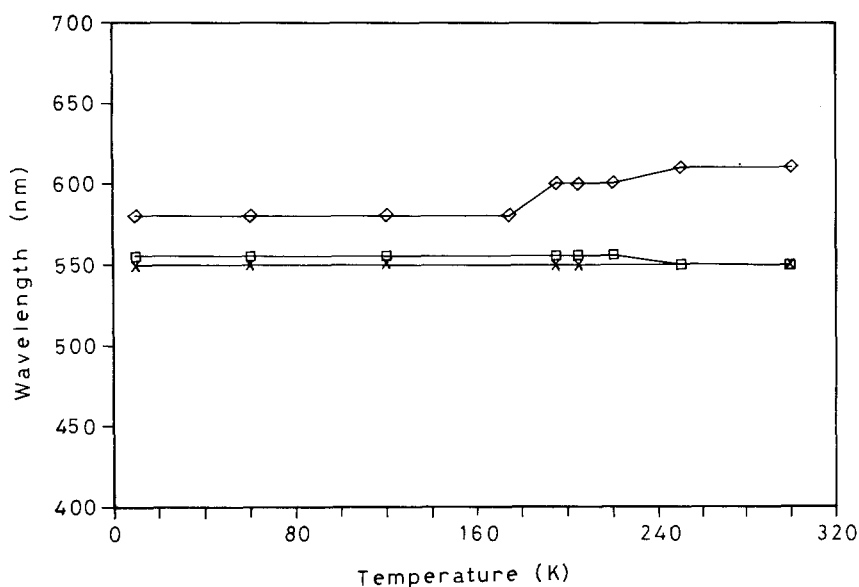
Fig. 2. Crystal emission spectra at 12 K of  $\text{Re}(\text{CO})_3\text{Cl}(\text{triphenylphosphine})_2$  (top) and  $\text{Re}(\text{CO})_3\text{Cl}$  1,2-bis(diethylphosphinoethane) (bottom)

**Table 2.** Electronic emission maxima

Compound	Wavelength of excitation nm	Band maxima, $\text{cm}^{-1}$			
		Solution		Solid	
		298 K	10 K	298 K	10 K
$\text{ClRe}(\text{CO})_3(\text{triphenylphosphine})_2$	457	18 100	18 000	17 000	17 200
	488		18 000	17 000	17 000
	514 <sup>a</sup>		17 500	16 900	17 200
	351				17 000 <sup>b</sup>
$\text{ClRe}(\text{CO})_3(\text{tri-}i{p}\text{-tolylphosphine})_2$	457	18 000	18 200	18 200	17 200
	488		17 900	17 600	17 900
	514 <sup>a</sup>		17 200	17 200	17 200
	351				17 200 <sup>b</sup>
$\text{ClRe}(\text{CO})_3$ 1,2-bis(diethyl- phosphinoethane)	457			19 000	19 000
	488			18 000	18 000
	514 <sup>a</sup>			18 000	18 000
	351				18 800

<sup>a</sup> Interference from scattered light and/or the filter precludes exact measurement

<sup>b</sup> A shoulder observed at about  $19\,200\text{ cm}^{-1}$  is probably caused by traces of  $\text{Re}(\text{CO})_5\text{Cl}$



**Fig. 3.** Comparison of the wavelength of the luminescence maximum of the rigidochromic molecule  $\text{Re}(\text{CO})_3\text{Cl}(1,10\text{-phenanthroline})$  (top trace) with those of  $\text{Re}(\text{CO})_3\text{Cl}(\text{triphenylphosphine})_2$  (middle) and  $\text{Re}(\text{CO})_3\text{Cl}(\text{tri-}i{p}\text{-tolylphosphine})_2$  (bottom) as a function of temperature in chloroform

## Discussion

The emission bands which are observed from the  $\text{Re}(\text{CO})_3\text{Cl}(\text{phosphine})_2$  complexes are assigned to a ligand field transition with a large triplet character [17–20]. In all of the samples studied here, the emission band overlaps the weak absorption band.

The extinction coefficients of these weak absorption bands are less than  $20 M^{-1} \text{ cm}^{-1}$ , consistent with a spin-forbidden d-d assignment.

The emission maximum of the parent compound  $\text{Re}(\text{CO})_5\text{Cl}$  is at  $19\,900 \text{ cm}^{-1}$  with a width at half height of  $5200 \text{ cm}^{-1}$  [12]. This band was assigned to the  ${}^1\text{A}^1(\text{e}^4\text{b}_2^2) \rightarrow {}^3\text{E}$  ligand field transition. Replacement of the chloride with a halide ligand lower in the spectrochemical series shifts the band maximum to lower energy. Replacement of two carbonyl ligands with two monodentate phosphine ligands or one bidentate phosphine ligand also causes a shift in the emission maximum to lower energy. The smallest shift is observed with the bidentate ligand (ca.  $1000 \text{ cm}^{-1}$ ) and the largest with the monodentate ligands (ca.  $2700 \text{ cm}^{-1}$ ). The emission energies and the magnitude of the shifts with ligand replacement are consistent with the ligand field assignment.

The emission of derivatives of the form  $\text{Re}(\text{CO})_3\text{Cl}(\text{phen})$  has been assigned to metal to ligand charge transfer transitions [2]. In these cases, empty  $\pi$  antibonding orbitals on the  $\alpha$ -diimine ligands lie lower in energy than the empty d orbitals on the metal. A charge transfer assignment is ruled out in the case of phosphine ligands for three reasons. First, the diethyldiphosphinoethane ligand does not contain any low lying ring  $\pi$  antibonding orbitals. Although the other phosphine ligands do have ring  $\pi$  antibonding orbitals which could participate in charge transfer interactions, the similarities of the energies of the transitions do not favor a change in assignment in going from 1,2-bis(diethylphosphinoethane) to triphenylphosphine. Second, the extinction coefficients of the lowest energy absorption bands are much too low for charge transfer transitions. In the cases of the  $\text{Re}(\text{Co})_3\text{Cl}(\text{diimine})$  complexes, the extinction coefficients of the lowest energy absorption bands are greater than  $10^3 M^{-1} \text{ cm}^{-1}$ . Finally, metal to phosphine charge transfer transitions in similar compounds generally occur higher in energy [1, 21]. In the case of the  $\text{Re}(\text{CO})_3\text{Cl}(\text{phosphine})_2$  compounds studied here, the charge transfer bands must lie at energies greater than  $33\,000 \text{ cm}^{-1}$ .

The luminescences of the phosphine complexes do not exhibit the rigidochromic effect. The term "luminescence rigidochromism" has been used to describe the substantial dependence of the emission maxima on the environmental rigidity [2]. Rigid media cause the emission maximum to blue shift and the emission intensity to increase relative to the spectra obtained from fluid solutions. This phenomenon is found for all the emissive Re systems studied in which the emission is attributed to a MLCT transition, but the origin has not yet been established [1, 2]. The shift which occurs when the solvent freezes is clear in case of the  $\text{Re}(\text{CO})_3\text{Cl}(1,10\text{-phenanthroline})$  as shown in Fig. 3. However, under the same conditions the phosphine complexes do not show a major shift.

The absence of a rigidochromic shift is probably attributable to the d-d nature of the emission. Ligand field excited states are much less sensitive to the environment of the molecule than are charge transfer states. On the other hand, charge transfer excited states are known to be very solvent sensitive, for example. The rigidochromic molecules containing the bipyridine and phenanthroline ligands and the non-rigidochromic phosphine complexes all have a similar electronic ground state. The results reported here suggest that the rigidochromism is caused primarily by changes in the energy of the MLCT excited state rather than by a large change in energy of the ground state.

## Acknowledgment

The author wishes to thank Prof. J. I. Zink for performing some of the measurements in his laboratory and for his valuable criticisms.

## References

- [1] Geoffroy G. L., Wrighton M. S. (1979) *Organometallic Photochemistry*. Academic Press, New York
- [2] Wrighton M. S., Morse D. L. (1974) *J. Am. Chem. Soc.* **96**: 998
- [3] Wrighton M. S., Morse D. L. (1975) *J. Organomet. Chem.* **97**: 405
- [4] Wrighton M. S., Morse D. L. (1976) *J. Am. Chem. Soc.* **96**: 998
- [5] Giordano P. J., Wrighton M. S. (1977) *Inorg. Chem.* **16**: 160
- [6] Abrahamson H. B., Wrighton M. S. (1978) *Inorg. Chem.* **17**: 3385
- [7] Luong J. C., Faltynsek R. A., Wrighton M. S. (1979) *J. Am. Chem. Soc.* **101**: 1597
- [8] Giordano P. J., Wrighton M. S. (1979) *J. Am. Chem. Soc.* **101**: 2888
- [9] Luong J. C., Faltynsek R. A., Wrighton M. S. (1980) *J. Am. Chem. Soc.* **102**: 7892
- [10] Westmoreland T. D., LeBozec H., Murray R. W., Meyer T. J. (1983) *J. Am. Chem. Soc.* **105**: 5952
- [11] McKiernan J., Pouxviel J.-C., Dunn B., Zink J. I. (1989) *J. Phys. Chem.* **93**: 2129
- [12] Wrighton M. S., Morse D. L., Gray H. B., Ottensen K. K. (1976) *J. Am. Chem. Soc.* **98**: 1111
- [13] Phillips J. R., Zink J. I. (1986) *Inorg. Chem.* **25**: 1503
- [14] Chang T. H., Zink J. I. (1986) *Inorg. Chem.* **25**: 2736
- [15] Abel E. W., Wilkinson G. (1959) *J. Chem. Soc.*: 1501
- [16] Tutt L., Zink J. I. (1986) *J. Am. Chem. Soc.* **108**: 5830
- [17] Cilizen M. M., Lees A. J. (1987) *J. Chem. Soc., Chem. Commun.*: 1752
- [18] Cilizen M. M., Lees A. J. (1988) *J. Am. Chem. Soc.* **110**: 6243
- [19] Cilizen M. M., Lees A. J. (1988) *J. Am. Chem. Soc.* **110**: 3892
- [20] Cilizen M. M., Lees A. J. (1989) *J. Am. Chem. Soc.* **111**: 6602
- [21] Dahlgren R. M., Zink J. I. (1977) *Inorg. Chem.* **16**: 3154

*Received September 29, 1992. Revised December 7, 1992. Accepted December 7, 1992*