STRUCTURAL AND PHOTOPHYSICAL PROPERTIES OF A MONONUCLEAR Re(I) COMPLEX: 
[P,N-{(C\textsubscript{6}H\textsubscript{3})\textsubscript{2}(C\textsubscript{5}H\textsubscript{5}N)P}Re(CO)\textsubscript{2}Br] 

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(Received: May 10, 2011 - Accepted: July 6, 2011)

**ABSTRACT**

We have prepared a new monometallic rhenium(I) carbonyl, the complex [P,N-{(C\textsubscript{6}H\textsubscript{3})\textsubscript{2}(C\textsubscript{5}H\textsubscript{5}N)P}Re(CO)\textsubscript{2}Br] by direct reaction of (Re(CO)\textsubscript{2}Br(THF)), and the ligand (C\textsubscript{6}H\textsubscript{3})\textsubscript{2}(C\textsubscript{5}H\textsubscript{5}N)P. The structure in the complex shows the pyridinic-phosphine ligand in a chelating mode, occupying cis positions around the rhenium octahedral environment. The molecule displays an absorption band centered at 315 nm which has been assigned to a MLCT transition, and a luminescence quantum yield of 0.001.

1.- INTRODUCTION

The phospine-type ligands having a second kind of coordinating atom or function have been of great interest in many areas of chemistry. The existence of a second coordinating motif with different properties, i.e. hardness, coordinating ability or trans-effect, add possibilities during a for example catalytic cycle, which could be used to tune the reaction to a specific target.\textsuperscript{1,6} Particularly, many attention have been devoted to the molecule diphenylpyridylphosphine, (C\textsubscript{6}H\textsubscript{3})\textsubscript{2}(C\textsubscript{5}H\textsubscript{5}N)P, synthesized 35 years ago (structurally determined in 1989). The molecule is a rigid bidentate ligand with a short bite of 2.5 Å (see scheme 1).

![Scheme 1](image)

Structures of monometallic complexes where the ligand exhibits a bidentate P,N (chelating) mode have been described for Ru,\textsuperscript{8-14} Pt,\textsuperscript{15,16} Te,\textsuperscript{17} Rh,\textsuperscript{12,18} Ni,\textsuperscript{19} W,\textsuperscript{20-22} Re,\textsuperscript{23-26} and Fe.\textsuperscript{27}

The complexes bearing Re(I) starts with (Ni(C\textsubscript{6}H\textsubscript{3})\textsubscript{2})(C\textsubscript{6}H\textsubscript{3})(C\textsubscript{5}H\textsubscript{5}N)P Re(CO)\textsubscript{2}X (X = Cl, Br),\textsuperscript{28} both examples presenting the pyridylidiphenylphosphine as a monodentate ligand coordinated through the phosphorous atom.

Rhenium(I) tricarbonyl diimine complexes, [Re(L)(CO)\textsubscript{2}(N,N)], have shown to have interesting photophysical and photochemical properties, which can be tuned modifying the kind of diimine ligand (N,N) or the L ligand (Cl, Br). These structural changes of the ligands have direct effect on the excited states character.\textsuperscript{29-30} Mononuclear rhenium complexes showing the ligand in a P,N-bidentate coordination mode includes [[(C\textsubscript{6}H\textsubscript{3})\textsubscript{2}P](P,N-C\textsubscript{6}H\textsubscript{3})(C\textsubscript{5}H\textsubscript{5}N)P]Re(NO)(Cl)\textsuperscript{2+}, [[P,N-(C\textsubscript{6}H\textsubscript{3})(C\textsubscript{5}H\textsubscript{5}N)P]Re(NO)(NO\textsubscript{3})\textsuperscript{2-}] and [[(C\textsubscript{6}H\textsubscript{3})\textsubscript{2}P](P,N-(C\textsubscript{6}H\textsubscript{3})(C\textsubscript{5}H\textsubscript{5}N)P]Re(NO\textsubscript{3})\textsubscript{2}Br\textsubscript{2}\textsuperscript{2+}].\textsuperscript{28} This latter species have been described to have an absorption band in the visible region at 479 nm which have been assigned as MLCT band and assigned with the help of TDDFT to a d → π*([C\textsubscript{6}H\textsubscript{3}](C\textsubscript{5}H\textsubscript{5}N)P) transition.\textsuperscript{28} To the best of our knowledge no reports of the emission properties have been reported for this kind of complexes. The present work reports the synthesis and photo-physical properties of a new rhenium complex, [P,N-{(C\textsubscript{6}H\textsubscript{3})\textsubscript{2}(C\textsubscript{5}H\textsubscript{5}N)P}Re(CO)\textsubscript{2}Br].

2.- EXPERIMENTAL

All reagents, (Re(CO)\textsubscript{2}(OC\textsubscript{2}H\textsubscript{3})Br), and (C\textsubscript{6}H\textsubscript{3})(C\textsubscript{5}H\textsubscript{5}N)P were used as provided from supplier (Aldrich), with no purification before use. Solvents were dried and freshly distilled before use. Standard Schlenck techniques were used for all manipulations.

i.- Synthesis of [P,N-{(C\textsubscript{6}H\textsubscript{3})\textsubscript{2}(C\textsubscript{5}H\textsubscript{5}N)P}Re(CO)\textsubscript{2}Br]. The compound was prepared by the direct reaction of (Re(CO)\textsubscript{2}(OC\textsubscript{2}H\textsubscript{3})Br), and (C\textsubscript{6}H\textsubscript{3})(C\textsubscript{5}H\textsubscript{5}N)P in the stoichiometric relation 1:2, according to the following scheme (Scheme 2):

![Scheme 2](image)

A yellow transparent solution of 187 mg of the ligand (0.72 mmol) in toluene was added dropwise to a colorless solution of 300 mg (0.36 mmol) of (Re(CO)\textsubscript{2}Br(THF)) dissolved in 20 mL of toluene. After completion of the addition, 20 mL of toluene were added. Reaction was allowed to continue during overnight with stirring. Toluene was then removed from the reaction mixture by evaporation at reduced pressure. A light yellow crude material was obtained. Crystal (X-rays diffraction quality) were obtained after recrystallization in a CH\textsubscript{2}Cl\textsubscript{2}/Hexane mixture (1:1). Yield 265,1 mg, 60.8 %.

**Anal. Calc.** for (C\textsubscript{6}H\textsubscript{3})(C\textsubscript{5}H\textsubscript{5}N)ReBrO: C, 39.16 %; H, 2.36 %; N, 2.28 %. Found: C, 39.12 %; H, 3.08 %; N, 2.29 %. Elemental analyses were obtained from Pontificia Universidad Catolica.

IR(cm\textsuperscript{-1}): 2026 (s), 1924(s), 1901(s), 1590(w), 1437(w), 1101(w).

**ii.- UV-Vis and Fluorescence spectroscopies.** UV-Vis spectra were recorded on an Agilent 8453 Diode-Array spectrophotometer in the range of 250-450 nm in aerated and deareated dichloromethane solutions. Emission spectra were measured in a Horiba Jobin-Yvon FluoroMax-4 spectrofluorometer at room temperature. The fluorescence quantum yields (Φp) were evaluated.
using quinine sulfate in 0.1 M H$_2$SO$_4$ (F$\_2$ = 0.55)$^{20,22}$ as actinometer. The optical densities of the sample (OD$_s$) and actinometer (OD$_{act}$) solutions were set below 0.15 and matched at the excitation wavelength. The quantum yield of the sample was calculated by using eq. 1:

$$\Phi_s = \Phi_{act} \left( \frac{I_s}{I_{act}} \right) \left( \frac{OD_{act}}{OD_s} \right) \left( \frac{h_{(s)}}{h_{(act)}} \right)$$

where $\Phi_{act}$ is the known quantum yield of the actinometer, $I_s$ and $I_{act}$ are the integrated fluorescence intensities for the sample and actinometer, and $h_s$ and $h_{act}$ are the refractive index of sample and actinometer solvents, respectively.

iii.- X-rays diffraction: The crystal structure of [P,N-{(C$_5$H$_5$)$_2$(CH$_2$N)P}Re(CO)$_2$Br] at room temperature was determined by X-rays diffraction, on a SMART CCD diffractometer using w-scans as collection strategy. Data collection was done on a SMART CCD diffractometer using w-scans as collection strategy. Data was reduced using SAINT,$^1$ while the structure was solved by direct methods, completed by Difference Fourier Synthesis and refined by least-squares using SHELXL.$^2$ Empirical absorption corrections were applied using SADABS.$^3$ The hydrogen atoms positions were calculated after each cycle of refinement of the model of the molecule as determined by X-ray diffraction.

The crystal structure of [P,N-{(C$_5$H$_5$)$_2$(CH$_2$N)P}Re(CO)$_2$Br] is the known quantum yield of the actinometer, I$_0$. The optical spectra for complex [P,N-{(C$_5$H$_5$)$_2$(CH$_2$N)P}Re(CO)$_2$Br] shows an intense band centered at 257 nm ($\epsilon = 1 \times 10^4$ M$^{-1}$ cm$^{-1}$), typical from a $\pi \rightarrow \pi^*$ transition.$^2$ The complex shows a broad absorption band in the UV-Vis region, with a maximum at 315 nm ($\epsilon = 5 \times 10^3$ M$^{-1}$ cm$^{-1}$), with a shoulder at around 355 nm. These bands can be assigned to a MLCT transition from a d-type metal orbital to a ligand $\pi^*$ orbital. The $\pi$-antibonding orbitals involved could correspond to carbonyl or diphenyl(2-pyridyl)phosphine ligands. In the

3.- DISCUSSION

i.- Structural Description: The complex [P,N-{(C$_5$H$_5$)$_2$(CH$_2$N)P}Re(CO)$_2$Br] corresponds to a mononuclear rhenium(I) complex. The coordination environment of the central rhenium atom, which could be well described as a distorted octahedron, is completed by three carbonyl carbon atoms in a face coordination, a bimide atom and phosphorous and nitrogen atoms from diphenylpyridylphosphine, the latter two showing a cis configuration, as required for its chelating bidentate coordination mode. Figure 1 shows a molecular structure diagram for the molecule as determined by X-ray diffraction.

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<th>Table 1. Crystal data and structure refinement for [P,N-{(C$_5$H$_5$)$_2$(CH$_2$N)P}Re(CO)$_2$Br]</th>
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Max. and min. $\Delta p$ = 2.573 and -1.393

ii.- Photophysical properties. Figure 2 shows the solution absorption spectra for complex [P,N-{(C$_5$H$_5$)$_2$(CH$_2$N)P}Re(CO)$_2$Br]. While the free ligand shows an intense band centered at 257 nm ($\epsilon = 1 \times 10^4$ M$^{-1}$ cm$^{-1}$), typical from a $\pi \rightarrow \pi^*$ transition,$^2$ the complex shows a broad absorption band in the UV-Vis region, with a maximum at 315 nm ($\epsilon = 5 \times 10^3$ M$^{-1}$ cm$^{-1}$), with a shoulder at around 355 nm. These bands can be assigned to a MLCT transition from a d-type metal orbital to a ligand $\pi^*$ orbital. The $\pi$-antibonding orbitals involved could correspond to carbonyl or diphenyl(2-pyridyl)phosphine ligands. In the
last case, phenyl or pyridyl rings have π-antibonding orbitals very close in energy as it have been shown by theoretical calculations of the more probably electronic transitions employing time-dependent density functional theory (TDDFT) methods.\textsuperscript{24,26} Its relatively low molar absorptivity is consistent with previous reports for this kind of transitions in similar complexes.\textsuperscript{18} This can be explained in terms of a rather small overlap between the d-orbital of the metal with the ligand π* ones.

![Figure 2. Absorption spectra for the ligand (C\textsubscript{6}H\textsubscript{5})\textsubscript{2}(C\textsubscript{5}H\textsubscript{3}N)P and the complex [P,N-\{(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}(C\textsubscript{5}H\textsubscript{3}N)P]Re(CO)\textsubscript{4}Br] (dashed line) measured in CH\textsubscript{2}Cl\textsubscript{2}.](image)

The band shows noticeably dependence with the solvent polarity towards shorter wavelengths (see supplementary Figure 1), which can be ascribed to a stabilizing effect of the solvent polarity over the molecular ground state.

The emission spectra of [P,N-\{(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}(C\textsubscript{5}H\textsubcript{3}N)P]Re(CO)\textsubscript{4}Br] determined by excitation at 315 nm displays a great Stokes shift (11200 cm\textsuperscript{-1}), with a maximum of emission at 550 nm, as shown in Figure 3. The same emission spectrum was obtained when the excitation wavelength was 355 nm. This is consistent with a great change of the molecular dipole moment of the excited state as it is typically found for other similar tricarbonyl rhenium complexes.\textsuperscript{19} The complex has a luminescence quantum yield of 0.001, compared with 0.095 for the free ligand. We did not observe any change in the measured quantum yield for the complex in the absence of oxygen, which is consistent with a short lifetime, probably lower than nanoseconds, for the excited state. The very low emission intensity of the complex, in contrast with the high emission observed for the related rhenium(I) diimine carbonyls,\textsuperscript{25} could be ascribed to the higher conformational flexibility of the bidentate phosphine ligand compared to the rigidity of aromatic diimines.

![Figure 3. Emission spectra for [P,N-\{(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}(C\textsubscript{5}H\textsubscript{3}N)P]Re(CO)\textsubscript{4}Br] (dashed line) and (C\textsubscript{6}H\textsubscript{5})\textsubscript{2}(C\textsubscript{5}H\textsubscript{3}N)P (solid line).](image)

\textbf{4.- CONCLUSION}

The monometallic rhenium(I) carbonyl [P,N-\{(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}(C\textsubcript{5}H\textsubscript{3}N)P]Re(CO)\textsubscript{4}Br] was prepared by direct reaction of (Re(CO)\textsubscript{4}Br(THF)), with (C\textsubscript{6}H\textsubscript{5})\textsubscript{2}(C\textsubscript{5}H\textsubscript{3}N)P, displays the ligand in a bidentate mode around the rhenium(I) center. The molecule absorbs light band centered at 315 nm, assigned to a MLCT transition. The complex has a luminescence quantum yield of 0.001, which can be related to the conformational flexibility of the molecule compared to rigid aromatic diimines.

\textbf{5.- Supporting Information}

Crystal data in the cif format have been deposited in CSD under code CCDC824816.

\textbf{6.- ACKNOWLEDGEMENTS}

The authors gratefully acknowledge financial support from DI/UNAB DI-28-10/R and FB0807. AV es miembro de Financiamento Basal para Centros Científicos y Tecnológicos of Excellence FB0807.

\textbf{7.- REFERENCES}

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