

STRUCTURAL AND PHOTOPHYSICAL PROPERTIES OF A MONONUCLEAR Re(I) COMPLEX: [P,N-((C₆H₅)₂(C₅H₅N)P)Re(CO)₃Br]

FELIPE VENEGAS,¹ NANCY PIZARRO,¹ ANDRES VEGA^{1,2*}

¹ Universidad Andres Bello, Facultad de Ciencias Exactas, Depto. Ciencias Químicas. Av. República 275, 3^{er} Piso

² Centro para el Desarrollo de la Nanociencia y la Nanotecnología, CEDENNA

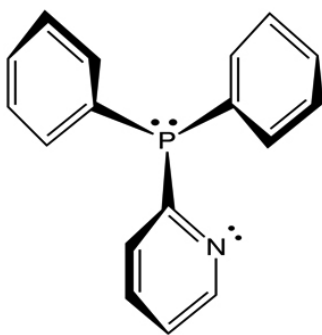
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ABSTRACT

We have prepared a new monometallic rhenium(I) carbonyl, the complex [P,N-((C₆H₅)₂(C₅H₅N)P)Re(CO)₃Br] by direct reaction of (Re(CO)₃Br(THF))₂ and the ligand (C₆H₅)₂(C₅H₅N)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 phosphine-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.¹⁻⁶ Particularly, many attention have been devoted to the molecule diphenylpyridylphosphine, (C₆H₅)₂(C₅H₅N)P, synthesized 35⁷ years ago (structurally determined in 1989⁸). The molecule is a rigid bidentate ligand with a short bite of 2.5 Å (see scheme 1).



Scheme 1.

Structures of monometallic complexes where the ligand exhibits a bidentate P,N (chelating) mode have been described for Ru,⁹⁻¹⁴ Pt^{15,16} Tc,¹⁷ Rh,^{12,18} Ni,¹⁹ W,²⁰⁻²² Re,²³⁻²⁶ and Fe.²⁷

The complexes bearing Re(I) starts with (N(C₂H₅)₄)[((C₆H₅)₂(C₅H₅N)P)Re(CO)₂X₂] or [(C₆H₅)₂(C₅H₅N)P₂Re(CO)₃X] (X = Cl, Br),²³ both examples presenting the pyridyldiphenylphosphine as a monodentate ligand coordinated through the phosphorous atom.

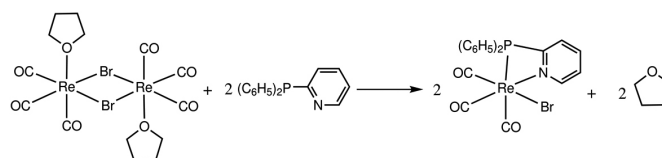
Rhenium(I) tricarbonyl diimine complexes, [Re(L)(CO)₃(N,N)], have shown to have interesting photophysical and photochemical properties, which can be tuned modifying the kind of diimine ligand (N,N) or the L ligand (Cl, Br). These structural changes of the ligands have direct effect on the excited states character.²⁸⁻³⁰ Mononuclear rhenium complexes showing the ligand in a P,N-bidentate coordination mode includes [(C₆H₅)₂P}P,N-(C₆H₅)₂(C₅H₅N)P}Re(NO)Cl₂]²⁴, [(P,N-(C₆H₅)₂(C₅H₅N)P)Re(CO)₃(NO)₃]²⁵ and [(C₆H₅)₂P}P,N-(C₆H₅)₂(C₅H₅N)P}Re(NO)_{0.87}Br_{2.13}]²⁶. 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*((C₆H₅)₂(C₅H₅N)P) transition.²⁶ 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-((C₆H₅)₂(C₅H₅N)P)Re(CO)₃Br].

2.- EXPERIMENTAL

All reagents, (Re(CO)₃(OC₄H₈)Br)₂ and (C₆H₅)₂(C₅H₅N)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-((C₆H₅)₂(C₅H₅N)P)Re(CO)₃Br]. The compound was prepared by the direct reaction of (Re(CO)₃(OC₄H₈)Br)₂ and (C₆H₅)₂(C₅H₅N)P in the stoichiometric relation 1:2, according to the following scheme (Scheme 2):



Scheme 2.

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)₃Br(THF))₂ 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 CH₂Cl₂/Hexane mixture (1:1). Yield 265,1 mg, 60.8 %.

Anal. Calc. for (C₂₀H₁₄NReBrO₃): 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 Católica.

IR(cm⁻¹): 2026 (s), 1924(s), 1901(s), 1590(w), 1437(w), 1101(w).

Infrared spectra in the 4000–400 cm⁻¹ region were recorded from KBr pellets on a Shimadzu Prestige 21 labstation FTIR available at Departamento de Ciencias Químicas, Universidad Andres Bello.

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 deaerated dichloromethane solutions. Emission spectra were measured in a Horiba Jobin-Yvon FluoroMax-4 spectrofluorometer at room temperature. The fluorescence quantum yields (Φ_F) were evaluated

using quinine sulfate in 0.1 M H₂SO₄ ($F_f = 0.55$)^{31,32} 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:

$$\Phi_S = \Phi_{ACT} \left(\frac{I_S}{I_{ACT}} \right) \left(\frac{OD_{ACT}}{OD_S} \right) \left(\frac{\eta_S^2}{\eta_{ACT}^2} \right) \quad (1)$$

where Φ_{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_ν and η_{ACT} are the refractive index of sample and actinometer solutions.

iii.- X-rays diffraction: The crystal structure of [P,N-((C₆H₅)₂(C₅H₅N)P)Re(CO)₃Br] at room temperature was determined by X-rays diffraction, on a prismatic 0.45 x 0.35 x 0.30 mm³ single crystal. Data collection was done on a SMART CCD diffractometer using ω -scans as collection strategy. Data was reduced using SAINT,³³ while the structure was solved by direct methods, completed by Difference Fourier Synthesis and refined by least-squares using SHELXL.³⁴ Empirical absorption corrections were applied using SADABS.³⁵ The hydrogen atoms positions were calculated after each cycle of refinement with SHELXL using a riding model for each structure, with C—H distance of 0.93 Å. $U_{iso}(H)$ values were set equal to 1.2 U_{eq} of the parent carbon atom. Additional data collection and refinement details are given in Table 1.

Table 1. Crystal data and structure refinement for [P,N-((C₆H₅)₂(C₅H₅N)P)Re].

FW/uma	613.40
Crystal System	Monoclinic
Space Group	P2 ₁ /n
a (Å)	10.141(1)
b (Å)	14.007(1)
c (Å)	14.931(1)
β (°)	92.378(1)
V (Å ³)	2119.2(3)
Z	4
d (g cm ⁻³)	1.923
μ (mm ⁻¹)	7.713
F000	1160
θ range	3.98 to 50.08
hkl range	-12 ≤ h ≤ 12
	-16 ≤ k ≤ 16
	-17 ≤ l ≤ 17
N_{tot}, N_{unq} (R_{int}, N_{obs})	12977, 3740 (0.024), 3415
Refinement Parameters	245
GOF	1.073
R1, wR2 (obs)	0.0292, 0.0328
R1, wR2 (all)	0.0695, 0.0711
Max. and min $\Delta\rho$	2.573 and -1.393

3.- DISCUSSION

i.- Structural Description: The complex [P,N-((C₆H₅)₂(C₅H₅N)P)Re(CO)₃Br] 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 *fac* correlation, a bromide 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.

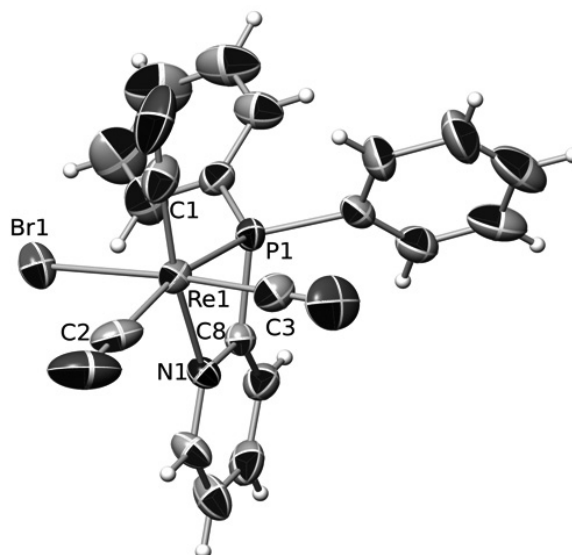


Figure 1. Molecular structure diagram for [P,N-((C₆H₅)₂(C₅H₅N)P)Re(CO)₃Br], showing partial atom numbering scheme. Displacement ellipsoids drawn at the 50% level of probability.

The Re1—N1 distance is 2.201(4) Å, a rather long distance compared to the 2.187(3) Å described for [((C₆H₅)₃P)₂(P,N-(C₆H₅)₂(C₅H₅N)P)Re(NO)Cl]₂²⁴, which was claimed as a long distance compared to the sum of the covalent radii, 2.08 Å,²⁴ or the average of the rhenium nitrogen distance in *mer*-[(C₆H₅N)₃ReX₃], 2.12 Å.³⁶ This has been attributed in [((C₆H₅)₃P)₂(P,N-(C₆H₅)₂(C₅H₅N)P)Re(NO)Cl]₂²⁴ to the *trans* effect of the carbonyl groups.³⁷ On the same sense, the carbonyl trans to the triphenylphosphine shows the longer distance, 1.949(6) Å, compared to the other two almost identical values, 1.899(6) and 1.904(6) Å. The biting N1—Re1—P1 angle is 64.9(1)°, far from the 90° expected for a regular octahedron, reflects the steric demand of the short bite of the ligand. Table 2 shows a summary of selected bond lengths and angles for [P,N-((C₆H₅)₂(C₅H₅N)P)Re(CO)₃Br].

Table 2. Bond distances (Å) and angles (°) for [P,N-((C₆H₅)₂(C₅H₅N)P)Re(CO)₃Br].

Re1—N1	2.201(4)	Re1—C1	1.899(6)
Re1—P1	2.5037(13)	Re1—C2	1.949(6)
Re1—Br1	2.6187(6)	Re1—C3	1.904(6)
N1—Re1—Br1	85.53(10)	P1—Re1—Br1	90.09(3)
N1—Re1—P1	64.93(10)	N1—C8—P1	104.6(3)
C1—Re1—N1	167.6(2)	C1—Re1—P1	102.7(2)
C2—Re1—N1	100.2(2)	C2—Re1—P1	165.1(2)
C3—Re1—N1	91.4(2)	C3—Re1—P1	91.3(2)
C1—Re1—Br1	94.2(2)	C1—Re1—C2	92.2(3)
C2—Re1—Br1	87.6(2)	C1—Re1—C3	89.4(3)
C3—Re1—Br1	175.8(2)	C2—Re1—C3	90.0(3)

ii.- Photophysical properties. Figure 2 shows the solution absorption spectra for complex [P,N-((C₆H₅)₂(C₅H₅N)P)Re(CO)₃Br]. While the free ligand shows an intense band centered at 257 nm ($\epsilon = 1 \times 10^4$ M⁻¹cm⁻¹); typical from a $\pi - \pi^*$ transition,³² the complex shows a broad absorption band in the UV-Vis region, with a maximum at 315 nm ($\epsilon = 5 \times 10^3$ M⁻¹cm⁻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 π^* orbital. The π -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 has been shown by theoretical calculations of the more probably electronic transitions employing time-dependent density functional theory (TDDFT) methods.^{24,26} Its relatively low molar absorptivity is consistent with previous reports for this kind of transitions in similar complexes.³⁸ This can be explained in terms of a rather small overlap between the d-orbital of the metal with the ligand π^* ones.

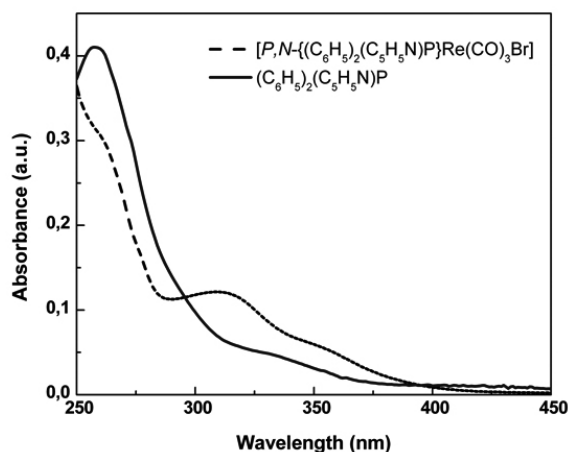


Figure 2. Absorption spectra for the ligand $(C_6H_5)_2(C_5H_5N)P$ (solid line) and the complex $[P,N-((C_6H_5)_2(C_5H_5N)P)Re(CO)_3Br]$ (dashed line) measured in CH_2Cl_2 .

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 $[P,N-((C_6H_5)_2(C_5H_5N)P)Re(CO)_3Br]$ determined by excitation at 315 nm displays a great Stokes shift (11200 cm^{-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 compared with the ground state, which could be rationalized in terms of large geometrical distortion of the excited state as it is typically found for other similar tricarbonyl rhenium complexes.³⁹ In contrast, the free ligand emits at 386 nm, with a small Stokes shift. The quantum yield for the complex emission is $\Phi = 0.001$, compared with $\Phi = 0.095$ 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,³⁰ could be ascribed to the higher conformational flexibility of the bidentate phosphine ligand compared to the rigidity of aromatic diimines.

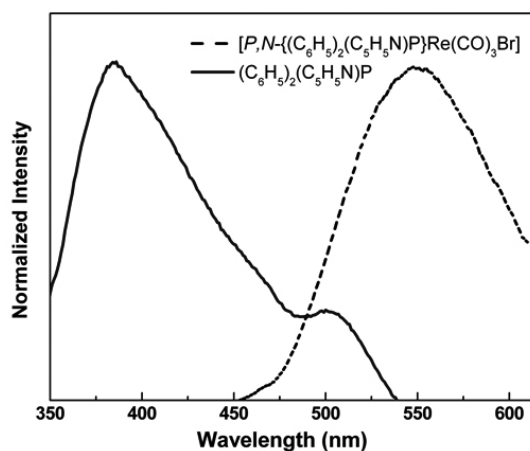


Figure 3. Emission spectra for $[P,N-((C_6H_5)_2(C_5H_5N)P)Re(CO)_3Br]$ (dashed line) and $(C_6H_5)_2(C_5H_5N)P$ (solid line).

4.- CONCLUSION

The monometallic rhenium(I) carbonyl $[P,N-((C_6H_5)_2(C_5H_5N)P)Re(CO)_3Br]$, prepared by direct reaction of $(Re(CO)_3Br)(THF)_2$ with $(C_6H_5)_2(C_5H_5N)P$, 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.

5.- Supporting Information

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

6.- ACKNOWLEDGEMENTS

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