

STRUCTURE OF *fac*-[(ppyEt)Re(CO)₃Br], A MONONUCLEAR Re^I COMPLEX DERIVED FROM PYRROLINE-PYRAZOLYL-PYRIDAZINE

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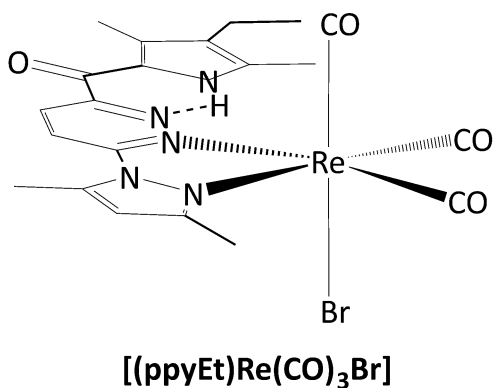
ABSTRACT

The reaction of 6-(1H-3,5-dimethylpyrazolyl)pyridazine-3-carboxylic acid with oxalyl chloride and then 2,4-dimethyl-3-ethylpyrrole leads to [6-(3,5-dimethyl-1H-pyrazol-1-yl)pyridazin-3-yl](4-ethyl-3,5-dimethyl-1H-pyrrol-2-yl)methanone (**ppyEt**). The reaction of **ppyEt** with bromotricarbonyl(tetrahydrofuran)-rhenium(I) dimer leads to [(ppyEt)Re(CO)₃Br] compound. The molecule of [(ppyEt)Re(CO)₃Br] displays a non-regular octahedron around the rhenium(I) center with a bromide. The molecule defines an intramolecular hydrogen bond between the 4-ethyl-3,5-dimethyl-1H-pyrrol-2-yl hydrogen atom and one nitrogen from the pyridazin-3-yl fragment with D...A 2.833(17) Å. The coplanarity of the 4-ethyl-3,5-dimethyl-1H-pyrrol-2-yl-carbonyl is attributed to this intramolecular bond, in addition to C—H...O=C and N—H...O=C interactions as suggested by NCI calculations.

Keywords: Rhenium(I), pyrazolyl, pyrrolyl, complex, non-covalent interactions.

1. INTRODUCTION

Rhenium(I) tricarbonyl complexes with diimines have attracted the attention of researchers during the last decades because of their useful photophysical properties, well-behaved and predictable synthesis, stability and potential applications [1-3]. Potential applications ranges from photosensitization [4-8], anion sensing [9, 10], biolabeling and therapy [11-15], to carbon dioxide photoreduction [5, 16-23]. They typically exhibit light absorption in the UV-Vis region, mainly from metal to ligand charge transfer (MLCT) transitions [24-26]. Pyrazolyl derivatives are appealing candidates to be explored, mainly due to their planarity and limited conformational flexibility that will diminish non-radiative deactivation paths [27, 28]. We have recently shown that substitution modifications over this skeleton would modulate the electronic structure and in consequence, the compound properties [29, 30]. Thus, this kind of compounds provides unique opportunities to rationally address their properties by finely tuning through modification of the ligands. Moreover, an interesting group of ligands based on pyrromethenyl (**ppyEt**) has been prepared and characterized [31]. To the best of our knowledge no previous examples of pyrrolyl-pyrazolyl-pyridazine tricarbonyl Re^I compounds have been reported. In the present article we describe the synthesis of the **ppyEt** ligand and the corresponding *fac*-[(ppyEt)Re(CO)₃Br] complex (see Scheme 1). This was obtained by direct reaction between **ppyEt** ligand and bromotricarbonyl(tetrahydrofuran)-rhenium(I). In addition to the structural characterization, DFT calculations were done in order to test the effect of intramolecular interactions on the conformation of the molecule.



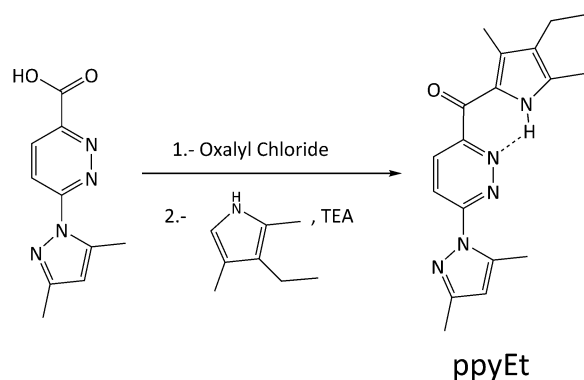
Scheme 1. Schematic structure of [(ppyEt)Re(CO)₃Br].

2. EXPERIMENTAL

Reagents. All reagents, (Re(CO)₅(OC₄H₈)Br)₂, BF₃·OEt₂, (COCl)₂, triethylamine were used as provided from supplier (Aldrich) and 6-(1H-3,5-dimethylpyrazolyl)pyridazine-3-carboxylic acid from Lifchemicals Inc. with no purification before use. Solvents were dried and freshly distilled before use. Standard Schlenck techniques were used for all manipulations.

i. Synthesis of [6-(3,5-dimethyl-1H-pyrazol-1-yl)pyridazin-3-yl](4-ethyl-3,5-dimethyl-1H-pyrrol-2-yl)methanone (ppyEt).

To 6-(1H-3,5-dimethylpyrazolyl)pyridazine-3-carboxylic acid (200 mg, 1 mmol) in 5 mL of dichloromethane (DCM, Seccosolv) was added 0.15 mL of oxalyl chloride (2 mmol) and few drops of dimethylformamide (DMF) at room temperature under stirring and argon atmosphere. The pale-yellow mixture was stirring during 1 h and the solvent was removed by evaporation. To the resulting, acid chloride dissolved in 10 mL of DCM was added drop to drop to a solution of 0.25 mL of 2,4-dimethyl-3-ethylpyrrole (2 mmol) in 2 mL of DCM, then, the mixture is allowed to react for 3 h at 55°C, the color changing slowly from pale brown to deep red. This solution at room temperature is mixed with 0.45 mL of triethylamine (3.5 mmol) following for the addition of boron trifluoride etherate (0.113 mL, 1 mmol) resulting a purple solution. The mixture was stirring overnight, and the crude obtained was washed 3 times with saturated aqueous NaHCO₃. The organic layer was then dried over MgSO₄, collected by vacuum filtration and solvent was removed. Chromatography on silica gel gave the pure compound to yield 0.052 g of crude product according to Scheme 2 [32].



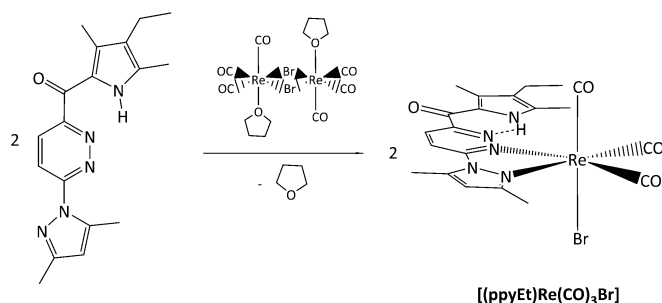
Scheme 2. Synthesis of **ppyEt**.

Anal. Calc. for (C₁₈H₂₁N₅O): C, 66.85, H, 6.55; N, 21.66. Found: C, 66.65 H, 5.95; N, 21.61 %.

¹H NMR (400 MHz, CDCl₃) The hydrogen peak from NH group belonging to pyrroline moiety is shown clearly at δ 11.9 ppm (s, 1H) while at 2.66 ppm (m, 2H) corresponding to -CH₂ and at 1.43 ppm (t, J = 7.6 Hz, 3H) related to -CH₃ from ethyl group of the same moiety. Hydrogen atoms from methyl groups of pyrroline ring were assigned to the peaks at 2.31 ppm (s, 3H) and 2.18 ppm (s, 3H). Respect to hydrogen nuclei from pyrazolyl ring, a singlet at 6.45 ppm (s, 1H) corresponding to -CH aromatic hydrogen and at 3.16 ppm (s, 3H) was assigned to the methyl group of position 15 from pyrazolyl ring (see H-NMR spectrum inset, Figure S3), finally, the last methyl group was related with the signal at 2.84 ppm (s, 3H). Protons from -CH pyridazine moiety were assigned to chemical shifts at 8.80 ppm (d, J = 8.9 Hz, 1H) and 8.66 ppm (d, J = 9.2 Hz, 1H) corresponding to hydrogen nuclei in positions 8 and 7, respectively.

ii. Synthesis of [(ppyEt)Re(CO)₃Br].

The compound was prepared by direct reaction of the **ppyEt** ligand (0.052 g, 0.160 mmol) with bromotricarbonyl(tetrahydrofuran)-rhenium(I) dimer (Aldrich, 0.064 g, 0.080 mmol) at room temperature in dichloromethane solution (Scheme 3). A dark brown solution was instantly obtained. Slow evaporation of the solvent at room temperature lead to solid brown material about 5%. Crystal (X-ray diffraction quality) were obtained after recrystallization in dichloromethane:acetone mixture (1:1).



Scheme 3. Synthesis of [(ppyEt)Re(CO)₃Br].

Anal. Calc. for (C₂₁H₂₁BrN₅O₄Re): C, 37.45; H, 3.14; N, 10.40. Found: C, 37.80; H, 2.90; N, 10.12 %.

Elemental analyses were obtained from Laboratorio Instrumental DCQ-Viña, Universidad Andres Bello. NMR analyses were collected at Facultad de Química y Biología, Universidad de Santiago.

iii. Structural Determination:

The crystal structure of [(ppyEt)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.[34-36] Empirical absorption corrections were applied using SADABS.[37] The data collection was done at 296 K. Since the statistics were considered rather poor, a new data set was measured at 100 K. All the data reported into the article corresponds to this low temperature determination unless stated. 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 or 0.96 Å and U_{iso}(H) of 1.2 or 1.5 times the parent atom. N—H distance was 0.86 and values were set equal to 1.2U_{eq} of the nitrogen atom into the room temperature structure, while the pyrrolic-nitrogen hydrogen atom was located into the Difference Fourier map and then refined with the constrain that the N—H distance was equal to 0.86 Å. Additional data collection and refinement details are given in Table 1.

iv. Computational details.

The wave function was generated at the DFT B3LYP/6-31+G(d,p) level of theory using the Gaussian09 Rev C.01 package of programs (G09)[38] by using the crystallographically determined coordinates as input. The LANL2DZ basis

set was used only for rhenium. The study of non-covalent interactions (NCI) and atoms in molecules (AIM) was carried out using the software MULTIWFN 3.7 multifunctional wavefunction analyzer [39]. Colour-filled iso-surfaces graphs were drawn using VMD 1.9.3 molecular visualization program,[40] while gnuplot 5.2.8 was used for 2D scatter plots of RDG [39]. Non-Covalent Interactions (NCI) is a recently developed technique based on the electron density and its derivatives that allows identification and visualization of noncovalent interactions [41]. Although requiring only molecular geometry information, NCI permits a substantial description of van der Waals interactions, hydrogen bonds, and steric repulsion in molecular complexes [42]. The NCI index is based on the reduced density gradient RDG(r) [43, 44]. The level of interaction is represented as a color scale in Figure 2 inset for simplicity [45].

Table 1. Crystal data and structure refinement for [(ppyEt)Re(CO)₃Br].

FW/uma	672.53
Crystal System	Monoclinic
Space Group	P2 ₁ /n
a (Å)	9.901(2)
b (Å)	12.083(3)
c (Å)	19.922(5)
β (°)	99.182(4)
V (Å ³)	2352.9(10)
Z	4
d (g cm ⁻³)	1.898
μ (mm ⁻¹)	6.90
F000	1292
θ range	2.0 to 26.0°
hkl range	-12 ≤ h ≤ 12
	-14 ≤ k ≤ 14
	-24 ≤ l ≤ 24
N _{tot} , N _{uniq} (R _{int}), N _{obs}	16779, 4619, 0.175, 2047
Refinement Parameters	299
GOF	1.10
R1, wR2 (obs)	0.062, 0.16
R1, wR2 (all)	0.1170, 0.1590
Max. and min Δρ	2.10 and -1.07

3. RESULTS AND DISCUSSION

3.1. Structural Description

Figure 1 shows the molecular structure of [(ppyEt)Re(CO)₃Br] as determined by X-ray diffraction. Table 2 displays main distances, angles and torsion angles. The coordination around the rhenium(I) center is a non-regular octahedron with a bromide, three carbonyl groups in facial correlation and the bidentate **ppyEt** ligand. The 3,5-dimethylpyrazolylpyridazine fragment remains highly planar as requested by the coordination to rhenium and previously described.[30]

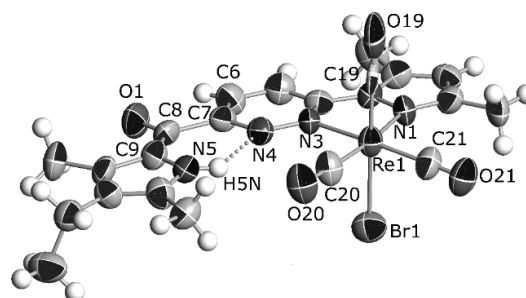


Figure 1. Molecular structure diagram for [(ppyEt)Re(CO)₃Br], showing partial atom numbering scheme. Displacement ellipsoids at the 50% level of probability for non-H atoms while hydrogens are drawn as arbitrary radii spheres. Interestingly, the 2,4-dimethyl-3-ethylpyrrolylcarbonyl substituent also remains coplanar with the pyridazine, as reflected by the low values of the torsion angles (N4—C7—C8—C9, 3(2)°, N4—C7—C8—O1, -178.5(1)°, C6—C7—C8—O1, -4.2(2)° and C6—C7—C8—C9, 177.5(1)°). This is ascribed to the existence of an intramolecular hydrogen bond between the pyrrolic hydrogen atom (H5N) and the uncoordinated pyridazinic nitrogen atom (N4) as detailed in Table 3, with D...A equal to 2.833(17) Å.

Table 2. Bond distances (Å) and angles (°) for [(ppyEt)Re(CO)₃Br].

Re1—C20	1.882(14)	Re1—N3	2.130(10)
Re1—C21	1.902(15)	Re1—N1	2.133(10)
Re1—C19	1.910(12)	Re1—Br2	2.5851(18)
C20—Re1—C21	87.7(6)	C19—Re1—N1	90.2(5)
C20—Re1—C19	92.1(6)	N3—Re1—N1	73.4(4)
C21—Re1—C19	91.2(5)	C20—Re1—Br2	92.2(5)
C20—Re1—N3	96.0(5)	C21—Re1—Br2	91.3(4)
C21—Re1—N3	174.2(5)	C19—Re1—Br2	175.1(4)
C19—Re1—N3	93.2(4)	N3—Re1—Br2	84.1(3)
C20—Re1—N1	169.2(5)	N1—Re1—Br2	85.2(3)
C21—Re1—N1	102.9(5)		
N4—C7—C8—C9	3(2)	N4—C7—C8—O1	-178.5(1)
C6—C7—C8—O1	-4.2(2)	C6—C7—C8—C9	177.5(1)

Table 3. Hydrogen-bond geometry (Å, °) for [(ppyEt)Re(CO)₃Br].

D—H...A	D—H	H...A	D...A	D—H...A
N5—H5N...N4	0.86	2.19	2.833(17)	131

In order to test the existence and magnitude of the intramolecular hydrogen bond detected by the X-rays, we have run NCI/AIM calculations based on the molecular structure determined for the molecule. Figure 2 shows the results of the NCI study for [(ppyEt)Re(CO)₃Br], where the color of the iso-surface indicates the force of non-covalent interaction, blue indicates hydrogen bond, green interactions of Van der Waals and red indicates the presence of a steric effect. By analyzing Figure 2, it is possible to find a single-color surface in blue, which corresponds to the hydrogen bond proposed based on the X-ray analysis (N5—H5N...N4). The AIM result is also consistent with this, as suggested by the critical point of bond (orange sphere) and to the bond path (orange line) between N5 and N4. There is also a critical point of ring (yellow sphere) within the N5-C9-C8-C7-N4 polygon. NCI results also suggest van der Waals interaction between a methyl hydrogen atom from pyrrolyl (H18C) and a carbonyl oxygen atom (O20) and between the pyrrolic nitrogen hydrogen atom (H5N) and a carbonyl hydrogen atom (O2). On the other hand, a critical point of ring within the polygon (marked in green and brown arrow), suggests a high stability in that region.

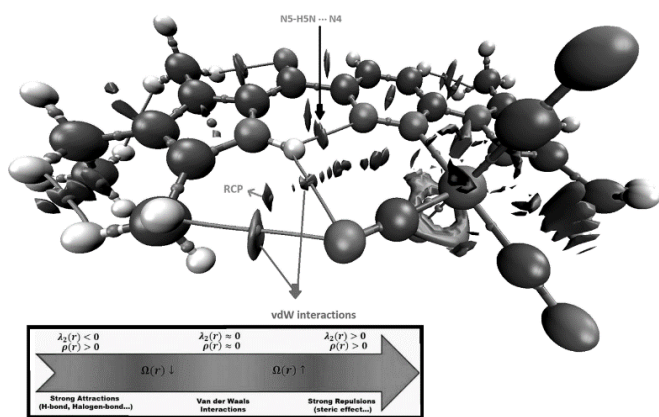


Figure 2. NCI molecular plot of non-covalent interactions with an isosurface $s = 0.5$ as computed for [(ppyEt)Re(CO)₃Br]. The orange, yellow, and purple spheres represent the bond critical points, ring critical points, and the cage critical points, respectively, while orange lines designate the bond paths. *Inset.* $\Omega(r)$ represents the product of sign of λ_2 (eigenvalue of electron density Hessian matrix at position r) and ρ (electron density).

4. CONCLUSION

The reaction of [6-(3,5-dimethyl-1H-pyrazol-1-yl)pyridazin-3-yl](4-ethyl-3,5-dimethyl-1H-pyrrol-2-yl)methanone (ppyEt) with bromotricarbonyl (tetrahydrofuran)-rhenium(I) leads to [(ppyEt)Re(CO)₃Br]. This last molecule displays a non-regular octahedron around the rhenium(I) center with a bromide, with ppyEt showing a high planarity. This is attributed to the existence of an

intramolecular hydrogen bond between the 4-ethyl-3,5-dimethyl-1H-pyrrol-2-yl hydrogen atom and one nitrogen from the pyridazin-3-yl fragment with $D\cdots A$ 2.833(17) Å, in addition to $C\cdots H\cdots O\equiv C$ and $N\cdots H\cdots O\equiv C$ interactions as suggested by NCI calculations. Because of this, it is expected that the absorption and emission bands of the complex shows the participation of the pyrrolyl π -system.

SUPPORTING INFORMATION

Crystal data in the cif format have been deposited in CSD under code CCDC1887186 (296 K) and CCDC18871867 (100 K).

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