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]methane (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-carbonyl and the corresponding bromide. 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 pyromethenyl (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.

2. EXPERIMENTAL

Reagents. All reagents, (Re(CO)3(OC8H18)Br)2, BF3·OEt2, (COCl)3, triethylamine were used as provided from supplier (Aldrich) and 6-(1H-3,5-dimethylpyrazolyl)pyridazine-3-carboxylic acid from Lifechemicals 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]methane (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 1. Schematic structure of [(ppyEt)Re(CO)3Br].

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1H NMR (400 MHz, CDCl3) The hydrogen peak from NH group belonging to pyrrole moiety is shown clearly at 6.19 ppm (s, 1H) while at 2.66 ppm (m, 2H) corresponding to -CH3 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 pyrrole 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) 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.

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 yield about 5%. Crystal (X-ray diffraction quality) were obtained after recrystallization in dichloromethane:acetone mixture (1:1).

The crystal structure of [(ppyEt)Re(CO)3]Br, 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 o-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 Uiso(H) of 1.2 or 1.5 times the parent atom. N-H distance was 0.86 and values were set equal to 1.2Uiso 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 constraint 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 MULTIMOFN 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].
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)Br], where the color of the is-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 (O2) and between the pyrrolinic nitrogen hydrogen atom (HNS) 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.

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

| Bond          | Distance (Å) | Angle (°) |
|---------------|--------------|-----------|
| Re1—C20      | 1.822(14)    |           |
| Re1—C21      | 1.902(15)    |           |
| Re1—C19      | 1.910(12)    | 2.5851(18)|
| C20—Re1—C21 | 87.7(6)      | 90.2(5)   |
| C20—Re1—C19 | 92.1(6)      | 73.4(4)   |
| C21—Re1—C19 | 91.2(5)      | 92.2(5)   |
| C20—Re1—N3  | 96.0(5)      | 93.4(4)   |
| C21—Re1—N3  | 174.2(5)     | 175.1(4)  |
| C19—Re1—N3  | 93.2(4)      | 91.3(4)   |
| C20—Re1—N1  | 169.2(5)     | 85.2(3)   |
| C21—Re1—N1  | 102.9(5)     |           |

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

| Bond           | Distance (Å) | Angle (°) |
|----------------|--------------|-----------|
| D—H•••A        | 0.86         | 2.19      | 2.833(17) | 131    |

**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 bromocarbonyl (teträhydrofuran)-rhenium(I) leads to \([(ppyEt)Re(CO)Br]\). 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—A 2.833(17) Å, in addition to C—H•••O=C and N—H•••O=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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