REDOX BEHAVIOR AND STRUCTURAL CHARACTERIZATION OF NITROSYL PINCER-TYPE PNP RHODIUM COMPLEXES

Carina Gaviglio[1*]; Fabio Doctorovich[2]; Juan Pellegrino[2]

[1] *Departamento de Física de la Materia Condensada, Gerencia de Investigación y Aplicaciones, Centro Atómico Constituyentes, CNEA.*
[2] *DQIAQF/INQUIMAE, FCEN-UBA/CONICET, Ciudad Universitaria, Pab. II, Buenos Aires, Argentina.*
* gaviglio@tandar.cnea.gov.ar

A topic of interest consists on exploring the combination of robust bulky pincer ligands that present high stability and steric protection with redox active ligands as NO in the reactivity of $\{RhNO\}^n$ complexes. Nitrosyl complexes are described as $\{MNO\}^n$ where *n* stands for the number of electrons in the metal d and π^* NO orbitals. In a previous work the activation of carbon-halogen bonds by a paramagnetic complex $\{RhNO\}^9$ with a PCP pincer type ligand was reported **[1]**. Herein the synthesis and characterization of a new paramagnetic complex $\{RhNO\}^9$ $\mathbf{1}^{+\bullet}$ with a PNP pincer type ligand is presented.

Reaction of $\{RhNO\}^8$ $\mathbf{1}^{2+}$ with 1 equivalent of $Co(Cp)_2$ in trifluorotoluene resulted in quantitative formation of $\mathbf{1}^{+\bullet}$ and $[Co(Cp)_2][BF_4]$. The paramagnetic nature of the one-electron reduced $\{RhNO\}^9$ species $\mathbf{1}^{+\bullet}$ was confirmed by EPR and by the broad resonances occurring in ^{1}H NMR. Also by FTIR the expected change was observed in the ν_{NO} upon the $\{RhNO\}^{8\rightarrow9}$ conversion from $\mathbf{1}^{2+}$ to $\mathbf{1}^{+\bullet}$ (1911 to 1650 cm^{-1}).

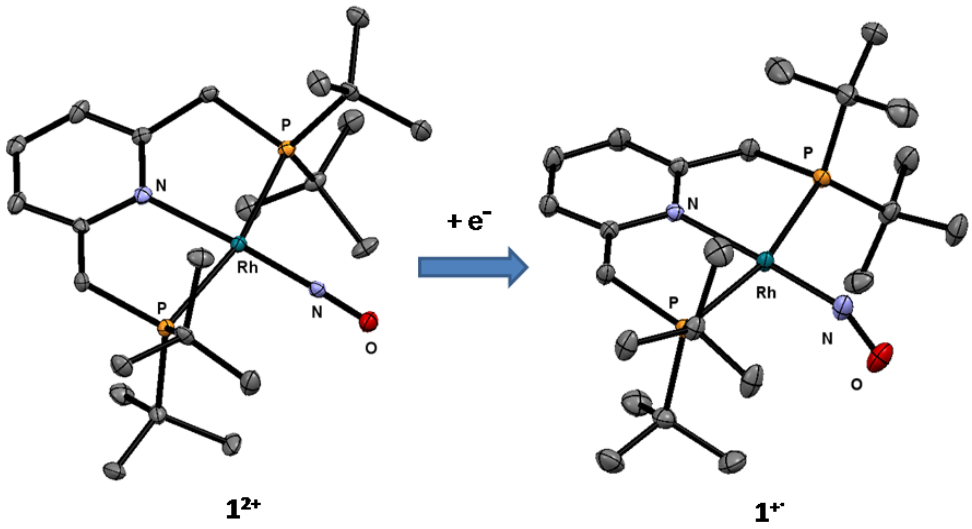

Figure 1: ORTEP plot of complexes $\mathbf{1}^{2+}$ and $\mathbf{1}^{+\bullet}$ at the 50% probability level. Hydrogen atoms and triflate counterions ($CF_3SO_3^-$) are omitted for clarity.

The molecular structure of both compounds $\mathbf{1}^{2+}$ and $\mathbf{1}^{+\bullet}$ was confirmed by X-ray diffraction (Figure 1). In both structures the rhodium atom is located in the center of a square-planar geometry with the nitrosyl group occupying the position *trans* to the *ipso* carbon. In $\mathbf{1}^{2+}$ the Rh-N-O angle is 176.1(3)º while in $\mathbf{1}^{+\bullet}$ is 145.5(2)º due to the more electron density on the NO ligand.

Palabras clave: nitrosyl complexes; DRX; redox behavior.

[1] J. Pellegrino, C. Gaviglio, D. Milstein, F. Doctorovich, Organometallics, 32 (2013) 6555–6564.