



## Sponsored by:



## A NOVEL NON-INNOCENT LIGAND REGULARIZES A FORMAL PALLADIUM(I) COMPLEX TO PALLADIUM(II)

D. R. Ramadan,<sup>a,b</sup> M. A. Fouad,<sup>a,b</sup> S. Miele,<sup>a</sup> F. Ferretti,<sup>a</sup> A. Brotons Rufes,<sup>c</sup> P. Macchi,<sup>d</sup> L. Sorace,<sup>e</sup> M. Gimferrer,<sup>f</sup> C. Costabile,<sup>\*c</sup> F. Ragaini<sup>\*a</sup>

<sup>a</sup> Dipartimento di Chimica, Università di Milano, Milano, Italy

<sup>b</sup> Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt.

<sup>c</sup> Dipartimento di Chimica e Biologia "A. Zambelli", Università di Salerno, Fisciano (SA), Italy

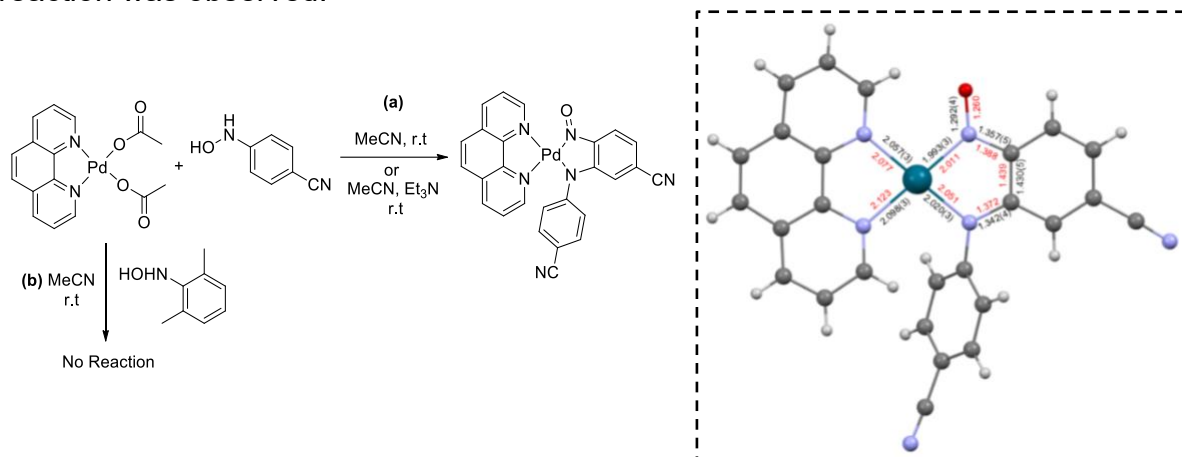
<sup>d</sup> Dipartimento di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano, Milano, Italy

<sup>e</sup> Dipartimento di Chimica "Ugo Schiff" & Udr INSTM Università di Firenze Sesto Fiorentino (FI), Italy

<sup>f</sup> Institut für Physikalische Chemie, Georg-August Universität, Göttingen, Germany

e-mail: fabio.ragaini@unimi.it

In the attempt to generate a palladium/phenanthroline complexes with an  $\eta^2$ -ArNO ligands preventing following reactions of the formed complex with excess nitrosoarene, we recently attempted to generate the desired complex by reaction of a palladium(II) precursor, Pd(Phen)(OAc)<sub>2</sub>, with *p*-cyanophenyl hydroxylamine. However, instead of the desired complex, a new paramagnetic complex was obtained and crystallographically characterized, in which two hydroxylamine-derived moieties have coupled to give an amido-nitrosoarene ligand. Considering the nitrosoarene as a neutral ligand and the amino group as an anionic one, as it is usually done, the complex would be a very rare example of monomeric palladium(I) complex. However, magnetic measurements and extensive theoretical calculations have shown that the unpaired electron actually resides on the nitroso group and the complex must be regarded as a palladium(II) complex with a radical dianionic ligand. Other arylhydroxylamines react in the same way, but when an *o,o*-disubstituted hydroxylamine was employed, no reaction was observed.



**Figure 1.** Reaction scheme and molecular structure of the product determined by single crystal X-ray diffraction. Relevant bond distances (in Å) are shown (calculated values in red).

**Acknowledgments:** The project was funded by the European Union - Next Generation EU, Mission 4 Component 1 CUP\_ G53D23003450006 and the University of Salerno (FARB). The single crystal diffraction experiment was carried out at the Next GAME Laboratory of the Politecnico di Milano, co-funded by Regione Lombardia.