



Seminario di Dipartimento
Venerdì 12 gennaio 2017 alle ore 14:30
aula C (primo piano VEC, Ed. Cannizzaro)

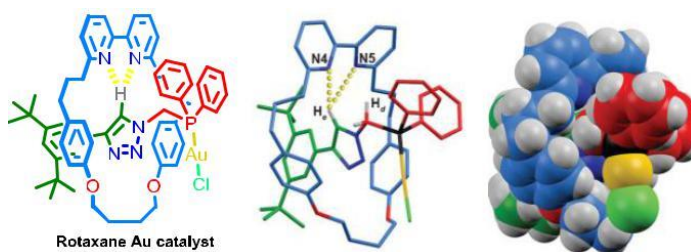
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A Stimuli Responsive Rotaxane Gold Catalyst

Abstract

Rotaxanes and catenanes are very appealing systems from several points of view.¹ They are easily functionalizable platforms that can be used to perform many different functions, such as sensors, molecular machines and catalysts.¹ The last one has attracted a lot



of attention in terms of the challenge to use these scaffolds to mimic enzymes, to perform processive motion and to switch on and off the catalytic activity of a specific site. Catalysts based on interlocked molecules have recently begun to receive attention.² For example, in the systems developed by Leigh and coworkers, the catalytic activity of a rotaxane is controlled by reversible shielding of organocatalytic moieties in the thread.³ Nevertheless, little is still known about the influence of the mechanical bond on the outcome of catalyzed reactions. An ambitious goal would be to influence the stereoselectivity in catalytic processes. In this view, a novel mechanically bonded gold-phosphine complex was synthesised using

a flexible AT-CuAAC approach.⁴ A widely explored Au^I-mediated reaction was then selected in order to investigate the effect of the mechanical bond on the catalytic behaviour of the novel rotaxane Au

complex.⁵ Although the non-interlocked thread readily mediates the process, the rotaxane requires a catalytically innocent guest (M), that binds inside the cavity forming a stable complex. It was demonstrated that the identity of the additive influences both the yield and diastereoselectivity of

the reaction.⁶ In conclusion, the first example of a rotaxane-based Au catalyst is now identified, paving the way towards a new approach to the development of stimuli responsive rotaxane-based metal catalysts. Future work will focus on the application of switchable rotaxanes as sensors and chiral ligands for enantioselective gold catalysis, an important and challenging aim in organic synthesis.

1 Crowley, J. D.; Goldup, S. M.; Lee, A.-L.; Leigh D. A.; McBurney, R. T. *Chem. Soc. Rev.* **2009**, *38*, 1530-1541.

2 Leigh, D. A.; Marcos, V.; Wilson, M. R. *ACS Catal.* **2014**, *4*, 4490-4497.

3 S. Hoekman, M. O. Kitching, D. A. Leigh, M. Pappmeyer, D. Roke *J. Am. Chem. Soc.* **2015**, *137*, 7656-7659.

4 Lahlali, H.; Jobe, K.; Watkinson, M.; Goldup S. M. *Angew. Chem. Int. Ed.* **2011**, *50*, 4151-4155.

5 Johansson, M. J.; Gorin, D. J.; Staben, S. T.; Toste, D. J. *Am. Chem. Soc.* **2005**, *127*, 18002-18003.

6 Galli, M.; Lewis, J. E. M.; Goldup, S. M. *Angew. Chem. Int. Ed.* **2015**, *54*, 13545-13549.