Deep Eutectic Solvents (*DES*) as New Green and Bio-Renewable Reaction Media for Metal-Catalyzed Organic Reactions

Joaquín García-Álvarez,[1,*] and Cristian Vidal.[1]

[1] *Laboratorio de Compuestos Organometálicos y Catálisis (Unidad Asociada al CSIC), Departamento de Química Orgánica e Inorgánica, Facultad de Química, Universidad de Oviedo, Oviedo, Spain – garciajoaquin@uniovi.es*

Keywords: Deep Eutectic Solvents, Homogeneous Catalysis, Isomerization of Allylic Alcohols.

One of the largest areas of consumption of petroleum-based chemicals in a conventional metal-catalyzed organic reaction is the solvent used as reaction media. Despite that the problems associated with conventional volatile organic solvents (*VOC's*) are well established, the use of green and bio-renewable solvents still remains a lasting challenge.[1] In this sense, the advantages of using Deep Eutectic Solvents (*DES*) as reaction medium is highlighted from the fact that they are bio-degradable, non-toxic, recyclable and could be easily prepared using inexpensive raw materials.[2-6]

Although *DES* have been explored in a variety of applications including metal deposition, metal oxide dissolutions, purification of bio-diesel, bio-transformations and different synthetic processes, their application in metal-catalyzed organic reactions has been barely notice, as far as we are aware.[4]

On the other hand, the search for organic reactions proceeding with efficiency, selectivity and atom economy, has emerged as a major goal in synthetic chemistry.[7-8] Isomerization reactions are typical examples of atom economic processes as no by products are generated. In this sense, the redox isomerization of readily accessible allylic alcohols is a useful and straightforward synthetic route to saturated carbonyl compounds, which are very important raw materials in organic chemistry.[9-12]

In this communication, and following our interest in studying the catalytic activity of ruthenium complexes in organic processes using non-conventional solvents (water and ionic liquids),[13] we will present, for the first time, the use of different *DES* [comprised of a mixture of a hydrogen bond donor (glycerol (*Gly*) or urea) with a simple halide salt (choline chloride, *ChCl*)], as totally green and bio-renewable solvents in the ruthenium catalyzed redox isomerisation of allylic alcohols,[14] proceeding with efficiency, selectivity and atom economy. It is important to note that this catalytic process displays: *i*) high activity under mild reaction conditions and low catalyst loading; *ii*) high yields in the absence of base, and *iii*) recyclability for four consecutive runs with only partial lost of activity.

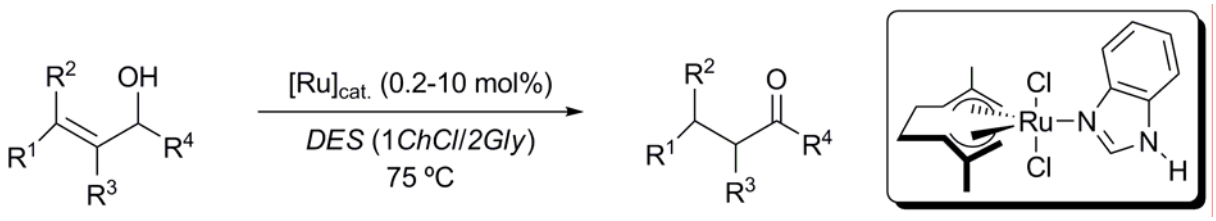

Fig. 1 – Ru(IV)-catalyzed isomerization of allylic alcohols using Deep Eutectic Solvents (*DES*) as green and bio-renewable solvents.

Acknowledgements

We are indebted to the Ministerio de Ciencia e Innovación (MICINN) of Spain (Consolider Ingenio 2010 (CSD2007-00006), CTQ2010-14796/BQU and RYC-2011-08541) for financial support. J.G.-A. thanks the MICINN and the European Social Fund for the award of a "Ramón y Cajal" contract.

References

1 *Handbook of Green Chemistry, Vols. 4, 5, and 6, Green Solvents*, Ed. P. T. Anastas; Wiley-VCH: Weinheim, Germany, 2011.

2 A. P. Abbott, R. C. Harris, K. S. Ryder, C. D'Agostino, L. F. Gladden, M. D. Mantle, *Green Chem.* 2011, **13**, 82.

3 D. Carriazo, M. C. Serrano, M. C. Gutiérrez, M. L. Ferrer, F. del Monte, *Chem. Soc. Rev*. 2012, **41**, 4996.

4 Q. Zhang, K. de Oliveira Vigier, S. Royer, F. Jérôme, *Chem. Soc. Rev.* 2012, **41**, 7108.
5 C. Ruβ, B. König, *Green Chem.* 2012, **14**, 2969.
6 M. Francisco, A. van der Bruinhorst, M. C. Kroon, *Angew. Chem. Int. Ed.* 2013, **52**, 3074.
7 B. M. Trost, *Science* 1991, **254**, 1471.
8 R. A. Sheldon, *Green Chem.* 2007, **9**, 1273.
9 L. Mantilli, C. Mazet, *Chem. Lett.* 2011, **40**, 341.
10 N. Alhsten, A. Bartoszewicz, B. Martín-Matute, *Dalton Trans.* 2012, **41**, 1660.
11 P. Lorenzo-Luis, A. Romerosa, M. Serrano-Ruiz, *ACS Catal.* 2012, **2**, 1079.
12 J. García-Álvarez, S. E. García-Garrido, P. Crochet, V. Cadierno, *Curr. Top. Catal.* 2012, **10**, 35.
13 J. García-Álvarez, J. Gimeno, F. J. Suárez, *Organometallics* 2011, **30**, 2893.
14 C. Vidal, F. J. Suárez, J. García-Álvarez, *Catal. Commun.*, 2013, *accepted manuscript*, DOI: 10.1016/j.catcom.2013.04.002.