Glycerol: A convenient green solvent and hydrogen donor for the ruthenium-catalyzed reduction of allylic alcohols

Alba E. Díaz-Álvarez, Pascale Crochet,∗ and Victorio Cadierno∗

Departamento de Química Orgánica e Inorgánica. Instituto Universitario de Química Organometálica “Enrique Moles” (Unidad Asociada al CSIC). Universidad de Oviedo. Julián Clavería 8, 33006 Oviedo, Spain – crochetpascale@uniovi.es

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During the last decade a large surplus of glycerol has been generated in manufacturing biodiesel fuel from vegetable oils since about 100 kg of this chemical per ton of biodiesel are formed. According to recent estimates,1 world-wide production of glycerol could have reached 2 million tons in 2010 and will grow in coming years due to the increasing demand of biodiesel, as well as the emergence of other large-scale processes based on the conversion of cellulose and lignocelluloses in which glycerol is also a by-product. Consequently, new applications for this polyol as a low-cost raw material need to be developed and/or the existing ones expanded.2

Due to its unique combination of physical and chemical properties, such as high polarity and boiling point, low toxicity and flammability, ability to form hydrogen bonds and to dissolve both organic and inorganic compounds (salts, acids, bases and metal complexes), and easy availability, glycerol as recently emerged as an economically appealing and safe solvent for organic synthesis.3 The growing interest of the chemical community in finding “green” solvents from renewable sources is also a prime motivation for the exponential growth of this research field.4

Herein, we would like to communicate that glycerol can be used as a green solvent and hydrogen donor in the ruthenium-catalyzed reduction of allylic alcohols, a tandem process that involves the initial reduct-isomerization of the allylic alcohol and subsequent transfer hydrogenation of the resulting carbonyl compound (Scheme 1).5

Among the different ruthenium sources employed, the best results were obtained with the hydrophilic arene-Ru(II) complex [RuCl2(η6-C6H6)(DAPTA)] (Figure 1), which associated with KOH is able to generate the corresponding saturated alcohols in high yields (up to 90%) and with almost complete selectivity in short times (6-15 h).

Figure 1 – Structure of the ruthenium(II) complex [RuCl2(η6-C6H6)(DAPTA)].

Interestingly, these reduction processes are also operative using technical grade glycerol and the catalyst could be recycled (up to 4 times) after simple extraction of the reaction products with diethyl ether.

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References