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Perspective

Titanocene dichloride: a new green reagent in organic chemistry

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Green reagents reduce or eliminate the use and generation of hazardous substances in the synthesis of chemical compounds [1]. The development of new green reagents is important for the development of a more sustainable chemical industry, based on processes that follow the principles dictated by green chemistry [2]. In this context, the use of green reagents, such as hydrogen peroxide and dimethyl carbonate, in reactions that can be driven by sunlight, have been widely developed over the past twenty years. Alternative methodologies have been implemented in chemical synthesis to catalyze reactions under safe and mild reaction conditions with the use of less harmful solvents and with reduced toxic waste production. Polymer supported reagents [3] have enabled many elegant and efficient strategies for performing a range of different transformations. The main advantage of polymer supported reagents is that excess reagent can be recovered by filtration and reused. However, many previously developed green reagents are applicable only to a very limited number of chemical transformations and substoichiometric amounts must be used.

In this paper, we highlight the effectiveness of Cp_2TiCl as a reagent that fulfils many of the principles of green chemistry, including high catalytic activity, low toxicity, high selectivity, and compatibility with environmentally benign solvents [4].

Cp_2TiCl, is a single electron transfer system (SET) obtained from non-hazardous materials such as Cp_2TiCl_2 and Mn or Zn [5]. Alternatively, organosilicon reducing agents can be used, thus avoiding reductant-derived metal waste [6]. Although, it is not a renewable feedstock, Cp_2TiCl, is derived from titanium, one of the most widely abundant and safe transition metals in the Earth's crust [7]. This reagent has been shown to be capable of promoting and/or catalyzing [8] homolytic cleavage of C-O, C-halogen, and O-O bonds, present in functional groups such as epoxides, ozonides, oxetanes, imines, halides, and carbonyl groups. A breakthrough in the application of this reagent was described by Gansäuer *et al.* [9] and Oltra *et al.* [10], with the development of two catalytic cycles, which allowed regeneration of Cp_2TiCl_2 from the titanium derivatives formed in homolytic cleavage of bonds (Figs. 1 and 2). The amount of Cp_2TiCl used in these catalytic cycles ranges between (5 and 20) mol%. Both catalytic cycles for epoxide ring opening are shown in Figs. 1 and 2.

In this context, both catalytic procedures minimize waste generation, contributing to the development of sustainable chemical processes. Although Mn or Zn is used as stoichiometric reagents (2–8 eq) both can be recovered by simple filtration. Furthermore, an economically attractive feature is that the collidine used in both catalytic cycles can be easily recovered during the reaction work-up by simple acid-base extraction [5]. Reactions catalyzed by this SET are conducted at atmospheric pressure and room temperature, which contributes

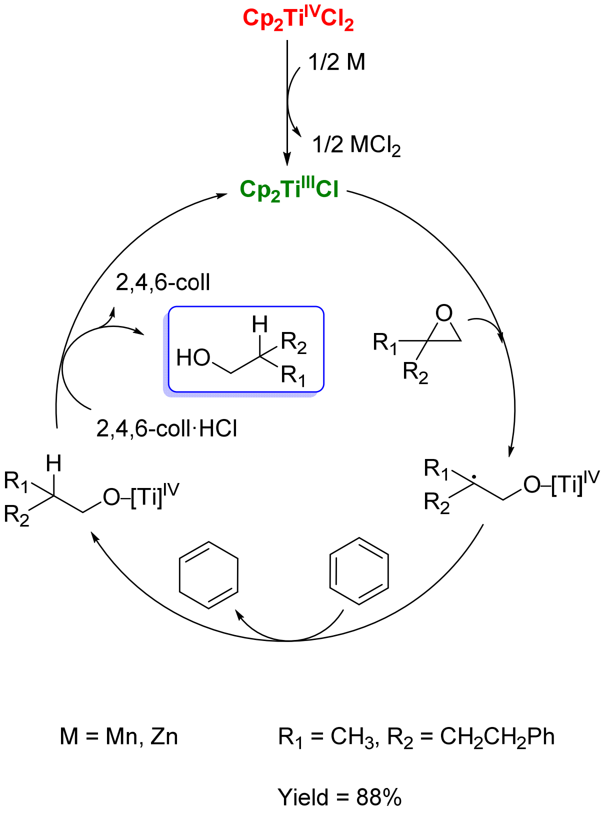

Fig. 1. Ti-catalyzed reductive epoxide ring-opening reactions.