Combined approaches to characterize the intermediates in alkyne cyclocarbonylations promoted by bioxazoline Pd(II) complexes, Annalisa Guerri,[a] Carla Carfagna,[b] Giuseppe Gatti,[b] Luca Mosca[b] and Paola Paoli,[a] [a]*Dept of Energy Engineering, University of Florence, Italy, and* [b]*Institute of Chemical Science, University of Urbino, Italy*. E-mail: a.guerri@ingfi1.ing.unifi.it

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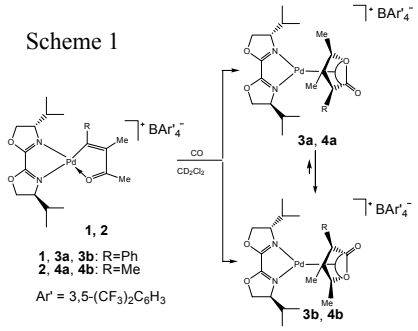
Palladium catalyzed cyclocarbonylation of unsaturated compounds is a powerful methodology which allows direct preparation of cyclic compounds containing a carbonyl group in the ring, starting from readily available substrates [1]. Among these kinds of reactions, cyclocarbonylation of simple alkynes in the presence of palladium(II) species represents a well-established pathway for the synthesis of γ-lactones [2]. We have recently demonstrated, through isolation of the reaction intermediates (one of them fully characterized by X-ray diffraction), that the elementary steps involved in this process are the acylpalladation of alkyne, followed by insertion of CO and cyclization to yield an α-diimine Pd complex in which the lactone moiety is coordinated in an η^3-allyl fashion [3]. The aim of the present work is to study the products of the reactions of palladacycles **1** and **2** containing an optically active bioxazoline ligand with CO (scheme 1).

Scheme 1



NMR and IR spectra revealed that, in each case, the reaction yields a mixture of two species in nearly equimolecular ratio, each one characterized by an η^3-allyl palladium structure containing a γ-lactone moiety. Particularly, each couple consists of two diastereoisomeric forms corresponding to the different coordinated face of the η^3-allyl ligand. Leaving the mixture in solution, the conversion of one isomer into the other was observed, reaching a diastereoisomeric excess of more than 90%. The steric and electronic factors responsible for the epimerization process were investigated through molecular modeling, EHMO and DFT calculations on model compounds. The reliability of the optimized structures was checked by a comparison with the solid state structures of analogous complexes. The aim is to understand how the chiral ligand could produce asymmetric induction in the cyclocarbonylation process, and to use this knowledge for the catalytic synthesis of enantiomerically pure γ-butenolides.

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