

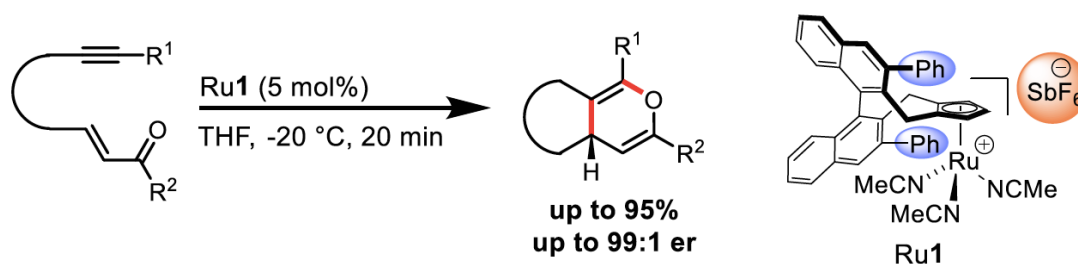
## Chiral Ruthenium-cyclopentadienyl Complexes as Versatile Catalysts for Enantioselective Transformations

David Kossler, Nicolai Cramer\*

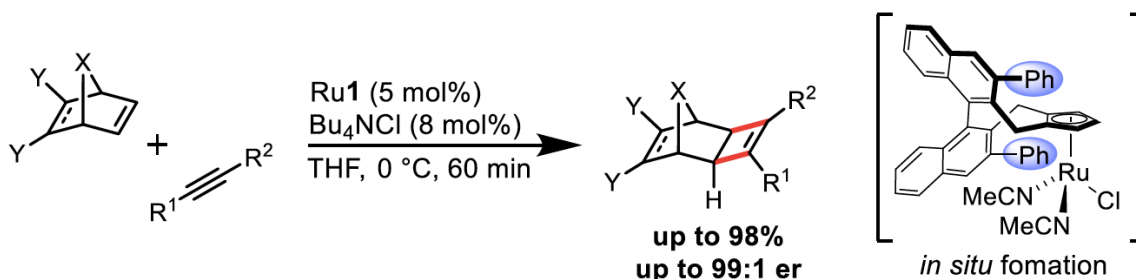
Laboratory of Asymmetric Catalysis and Synthesis, EPF Lausanne EPFL  
SB ISIC LCSA, CH-1015 Lausanne Switzerland nicolai.cramer@epfl.ch

The cyclopentadienyl (Cp) ligand is of fundamental importance for organometallic chemistry and as such found in countless transition-metal catalysts. Chiral versions of these catalysts often employed tethering strategies to the complexed metal, which goes to the expense of free coordination sites. Our group has developed chiral versions of these ligands, which keep the maximum number of coordination sites unoccupied and therefore available in the catalytic cycle.<sup>1</sup>

Ruthenium catalyzed cycloisomerizations offer a rapid access to complex molecular frameworks in an atom economical fashion.<sup>2</sup> Therefore the cationic  $[\text{CpRu}(\text{MeCN})_3]\text{PF}_6$  complex found widespread application in organic synthesis. Recently we reported the synthesis of a set of chiral cationic Ru(II) catalysts bearing our chiral  $\text{Cp}^X$  ligands and their application in the formal [4+2] cyclization of yne-enones to the corresponding pyrans in high enantioselectivity.<sup>3</sup>



In the course of this project we discovered a considerably large influence of the counterion on the reactivity and selectivity of the transformation. We opted to explore these effects with particular emphasis on covalently binding anions, thus obtaining a chiral congener of the well-established neutral  $\text{Cp}^*\text{Ru}(\text{cod})\text{Cl}$  catalyst. This idea proved to be feasible and led to the development of an asymmetric version the Ruthenium catalyzed formal [2+2] reaction of strained bicyclic alkenes with internal alkynes to chiral *exo*-cyclic cyclobutenes.<sup>4</sup>



(1) Newton, C. G.; Kossler, D.; Cramer, N. *J. Am. Chem. Soc.* **2016**, *138*, 3935.

(2) Trost, B. M.; Frederiksen, M. U.; Rudd, M. T. *Angew. Chem. Int. Ed.* **2005**, *44*, 6630.

(3) Kossler, D.; Cramer, N. *J. Am. Chem. Soc.* **2015**, *137*, 12478.

(4) a) Mitsudo, T.-a.; Naruse, H.; Kondo, T.; Ozaki, Y.; Watanabe, Y. *Angew. Chem. Int. Ed.* **1994**, *33*, 580; b) Kossler, D.; Cramer, N. *manuscript submitted*.