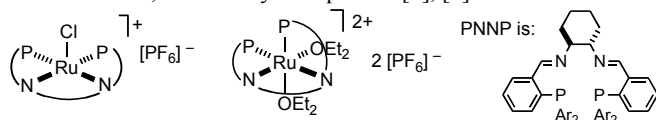


## Understanding Stereoselective Atom-transfer Reactions of Chiral Ruthenium Complexes

Antonio Mezzetti, Dept Chem. & Appl. Biosciences, ETH Zurich, CH.  
E-mail: mezzetti@inorg.chem.ethz.ch

In an atom-transfer reaction, a group or atom (carbene, oxygen, fluorine) is transferred *to* or *from* a noncoordinated molecule. We are studying ruthenium complexes with chiral tetradentate PNNP ligands that catalyze such reactions, *e. g.*, the asymmetric cyclopropanation and epoxidation of olefins and the electrophilic hydroxylation and fluorination of 1,3-dicarbonyl compounds [1], [2]:



The structural properties of the intermediates (either carbene or enolato complexes) of the catalytic cycle help explain the observed diastereo- and enantioselectivity. As such intermediates are very reactive, most structural information derives from molecular modeling calculations rather than from crystallographic studies. Nonetheless, crystallography is indispensable as a starting point and to validate the MM methods used.

Carbene transfer from  $[\text{RuCl}(\text{CHCO}_2\text{R})(\text{PNNP})]^+$  to uncoordinated styrene and the attack of electrophilic F- and O-donors onto the enolato complexes  $[\text{Ru}(\text{O}-\text{O})(\text{PNNP})]^{n+}$  ( $n = 1$  or  $2$ ) will be discussed.

[1] Bachmann S., Furler M., Mezzetti A., *Organometallics*, 2001, **20**, 2102. [2] Toullec P.Y., Bonaccorsi C., Mezzetti A., Togni A., *Proc. Natl. Acad. Sci. USA*, 2004, **101**, 5810.

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