

# In-situ Insights into the Activation Process of Cyclopentadienyl Ruthenium Dicarbonyl Complexes Used in Racemization of *sec*-alcohols

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The  $\eta^5$ -Ph<sub>5</sub>CpRu(II)(CO)<sub>2</sub>Cl-type complexes have been successfully applied as in-situ racemization catalyst in chemoenzymatic dynamic kinetic resolution of *sec*-alcohols.<sup>1,2</sup> Although these catalysts are already widely investigated, some aspects of their activation mechanism deserves to be enlightened. Therefore in this work our intention was to reveal the mechanistic pathway with the help of in-situ XAFS spectroscopy.

The activation process of the catalysts were followed by in-situ Ru K-edge (22117 eV) EXAFS, performed at beamline P64 at Petra III Extension, Hamburg, Germany. The reactions were carried out in a custom made temperature controlled glass reactor<sup>3</sup> at room temperature. In order to increase the solubility of the catalysts anhydrous THF was used as solvent, which also slowed down the reaction rate to a convenient range to study. Besides the original  $\eta^5$ -Ph<sub>5</sub>CpRu(II)(CO)<sub>2</sub>Cl catalyst, three analogues (substituted on the phenyl ring in para-position with -MeO, -F or -CF<sub>3</sub> groups) were studied as well.

The edge position did not change during the activation, indicating that the oxidation state remained +2 during the whole process. However, the coordination environment of the Ru notably transformed, as systematic and significant changes were observable both in the XANES and in the EXAFS spectra. The activation is proposed to go through an intermediate state, which was identified as a charged acyl-type complex, with one CO and the Cl<sup>-</sup> still coordinating to the Ru(II). This species is almost instantly formed after the addition of the *tert*-BuOK, which was used as an activating agent. The lifetime of this intermediate varies between 20 min and one day, strongly depending on the substituent of the phenyl rings. With sufficiently strong electron withdrawing substituents like the -CF<sub>3</sub> group the whole reaction can be quenched at this state. This complex then continuously transforms into the active species via losing the chloride meanwhile the Ru(II) coordinates the *tert*-butoxi group, and both of the two original carbon-monoxides. The Ph<sub>5</sub>Cp ring remains unaffected during the activation reaction.

With these in-situ XAFS measurement we experimentally proved the existence of the acyl-type intermediate during the activation of the  $\eta^5$ -Ph<sub>5</sub>CpRu(II)(CO)<sub>2</sub>Cl racemization catalyst, which was previously claimed by IR measurements and quantum chemical calculations.

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