

## Abstract

In the present work chiral and non chiral metallophosphonates are synthesized and applied as Umpolung catalysts in cross-benzoin reaction, to investigate the correlation between structure of catalyst and reactivity / enantioselectivity. Chiral systems fenchone-based phosphonates are applied as precatalysts in the cross-benzoin reaction. Thereby yields up to 92% and enantioselectivities up to 54% ee are obtained. For this type of catalysis a significant rise in reactivity is achieved in the catalysis when using a precatalyst with CF<sub>3</sub>-substituents in  $\alpha$ -position. The effect of CF<sub>3</sub>-groups on reactivity is further investigated by the application of different fluorinated precatalysts. Therefore fluorinated and nonfluorinated cyclic six-, seven-, and nine-membered ring phosphonates are synthesized and applied in the cross-benzoin reaction. The CF<sub>3</sub>-substituted phosphonates achieve lower yields compared to the analog hydrogen substituted phosphonates. This investigation leads to the conclusion that electron withdrawing CF<sub>3</sub>-groups stabilize the catalyst-substrate-adduct and the carbenium intermediate, whereas stronger stabilization leads to a reduction of reactivity respectively. Furthermore the influence and the necessity of the metal cation in the metallophosphonate catalyzed cross-benzoin reaction are revealed. The use of different alkali metal (Li, Na, K, without) TADDOL phosphonates result in considerable higher yields in the presence of a counterion (14-39%) in comparison when no counterion (>5%) is used. Quantum mechanical investigations reveal that the alkali metal cation stabilizes the transition structures of the catalyst-substrate-adduct formation leading to the fact, that the Umpolung step becomes the rate determining step, which is contrary to the catalysis without using a counterion. The yields for the different alkali metal counterions result from stabilization intensity of this transition structure.