

# Quantum chemical investigations on iron (III) and copper (II) catalyzed Michael Reactions

Christoph van Wüllen, Silke Pelzer, and Julia Borowka

Institut für Chemie Sekr. C3; Technische Universität Berlin

Straße des 17. Juni 135; 10623 Berlin; Germany

The Michael reaction, a nucleophilic addition of enolates to acceptor-activated alkenes such as  $\alpha,\beta$  unsaturated carbonyl compounds, is an important C-C bond forming reaction in the toolbox of synthetic chemistry. Under base catalysis which is the classical reaction condition, oligomerization of the acceptor may occur, as well as unwanted aldol-type reactions within the product. This can be avoided if the reaction takes place in a neutral or acidic environment, which is possible with catalytic amounts of Lewis acidic metals.

We report our efforts to establish the reactive intermediates and thus the mechanism of the iron (III) catalyzed Michael addition of diketones [1]. Most likely, a single iron center is involved in the reaction but it carries two enolates, one of which is merely a spectator in the reaction. The inhibiting effect of chloride anions occurs because coordination of chloride increases the proton affinity of the coordinated enolate, eventually leading to a dissociation of the diketone from the metal center and formation of  $[\text{FeCl}_4]^-$  which is a thermodynamic sink in this system. Indeed, experiments have shown that chloride-free catalysts are operative in much lesser amounts.

Experimental attempts to find an enantioselective variant of this reaction through chiral co-ligands failed, but an enamine derivative made from the original diketone with a chiral  $\alpha$ -amino acid can be added to a Michael acceptor with high enantioselectivity. This reaction is best catalyzed by copper (II) acetate. Our results so far indicate that this reaction proceeds via a planar tetracoordinated copper center which is approached by the oxygen of the acceptor in the course of the reaction. Most likely, the C-C forming step is preceded by a proton transfer within the reactive complex from the enamine nitrogen to the acetate, such that the nucleophile in action is a coordinated aza enolate.

[1] S. Pelzer, T. Kauf, C. van Wüllen, and J. Christoffers,

J. Organomet. Chem. **684**, 308 (2003)