Dr. Kristine Müther

Abstract of the dissertation

“Generation, structure and reactivity of metallocene-stabilized silylium ions”

Silylium ions, formally tricoordinated cationic silicon compounds, have proven to be extremely strong Lewis acids, which were even able to coordinate to molecules that have not been considered as Lewis bases before. Due to this high reactivity *free* silylium ions – cations without any coordination to other Lewis bases – were not isolable in condensed phase for a long time. One possibility of stabilizing these species is the introduction of an intramolecularly available Lewis base. This stabilization is, for example, achieved by a suitable metallocene group attached in close proximity to the cationic silicon atom.

Kristine Müther’s dissertation focused on the synthesis, structure and reactivity of such metallocene-stabilized silylium ions. In this work, the crystallization of one of these highly reactive silicon compounds was accomplished by the selection of an appropriate counter anion. Furthermore, the structure of this ferrocene-stabilized silylium ion was unraveled by X-ray structural analysis for the first time. The molecular structure revealed an extreme dip angle of the silicon atom towards the iron atom of the ferrocene backbone. The bonding situation can be explained by two 3-centre-2-electron bonds, including the silicon atom, the iron atom and the ipso carbon atoms of both cyclopentadienyl ligands. This structural motif distinguishes the examined ferrocene-stabilized silylium ion from analogous carbenium ions and boranes, which are characterized by a substantially smaller dip angle and show no interaction with the lower cyclopentadienyl ring.

With the structural characterization of a ferrocene-stabilized silylium ion in hand, more derivatives with different substitution patterns at the silicon atom and at the ferrocene backbone as well as a first ruthenocene-stabilized cation were synthesized. The new silylium ions were characterized by ^{29}Si NMR spectroscopy and their Lewis acidity was investigated. Within these studies, a ligand scrambling reaction was observed for cations with small substituents at the silicon atom.

Furthermore, the use of ferrocene stabilized silylium ion as catalysts in organic synthesis chemistry was examined. The good performance of these silylium ions in catalysis was demonstrated in silylium ion-mediated hydrosilylation reactions. Both ketones and imines were identified as suitable substrates. The reactivity was mainly influenced by the hydride affinity of the intermediate silyl carboxonium or silyl iminium ions.