IMIDAZOLINIUM SALTS WITH NITRO GROUPS – SYNTHESIS AND APPLICATIONS

The aim of the presented dissertation comprised the synthesis of new imidazolinium salts with nitro groups and their application. These compounds, as precursors of *N*-heterocyclic carbenes (NHC), could enable to modify the ruthenium metathesis catalysts. Despite many years of improving the methodology and development of new complexes, all difficulties have not been overcome by scientists until today. The basic problem is the formation of a mixture of *E* and *Z* isomers, often difficult to separate, that complicates the synthesis of biologically active compounds (*e.g.* anticancer drugs or pheromones). Unsymmetrical NHC ligand coordinated with the ruthenium atom could a suitable geometry of metallacyclobutane intermediate formed during the metathesis, thus increasing *Z*-selectivity of the modified 2nd generation catalyst.

In the literature part of the doctoral thesis imidazolinium and imidazolium salts were presented (**Chapter 1**). These compounds are a precursors of *N*-heterocyclic carbenes (NHC), which are usually employed as ligands in ruthenium and palladium complexes, or as organocatalysts. Division, preparation and application of NHC carbenes were shown in **Chapers 2** and **3**. A very important issue raised in the **Chapter 4** is the characteristic, as well as modifications of the indenylidene metathesis catalysts.

The next part was divided into synthesis and application of imidazolinium salts with nitro groups. In the **Chapter 5** the synthesis of new unsymmetrical imidazolinium salts with mesityl and nitroaryl (dinitroaryl) substituents were described. As a results of the experiments salts with nitrophenyl (approach A), as well as nitrobenzyl (approach B) moiety were obtained. In case of approach B the synthesis of dinitrobenzyl salt was also successful. Further studies included the synthesis of imidazolium salts with mesityl and nitroalkyl group. Unsymmetrical imidazolium salts with the steroidal substituent were also synthesized. A number of alkyl derivatives of imidazolium salts were also obtained, as well as 4-nitroimidazolium salt with a steroid moiety.

The next part of presented studies was devoted to the application of new salts (**Chapter 6**). The research performed has focused on the modification of 2nd generation ruthenium metathesis catalysts. It was related to the idea that unsymmetrically nitro-substituted NHC would create a charge-transfer complex with olefinic substrates and increase a possibility of their coordination to the ruthenium center from one side. As a result, the *all-cis* geometry in metallacyclobutane intermediate should be more preferred and products with Z-configurated double bonds can be achieved. Despite initial failures of the synthesis of catalysts caused by a weak nucleophilicity of the nitroaryl substituted NHC, syntheses of two indenylidene complexes with the NHC ligand substituted with the nitrobenzyl group were successful. The complexes were tested in RCM, en-yne cyclization and CM model reactions. Obtained catalysts were stable in standard laboratory conditions and non-sensitive to moisture. The geometry optimization of the molecules were determined by the static DFT calculations. Another modified metathesis catalyst having an interesting structure was inactive in the model metathesis reactions. However, after addition of an aqueous HCl its catalytic activity increased significantly. The complex exhibited the features of *'the latent catalysts'*. New complex successfully promoted metathesis in water, so it can be used in accordance with the idea of the green chemistry.

Imidazolium salts frequently show an interesting biological activity, therefore salts with the steroidal substituent were tested as antimicrobial agents. New salts proved active *in vitro* against some Gram(+) bacteria as well as fungi (*Candida albicans*). The activity of some of them was comparable to that of commercial antibiotics or even better, what indicates the possibility of their commercialization. The **Chapter 7** is a summary of the results of the research.

The last part (**Chapters 8 - 12**) presents a detailed description of syntheses of imidazolinium, as well as imidazolium salts with nitro groups. Additionally, the preparation of new olefin metathesis catalysts and substrates used in model metathesis reactions were given. The experimental part also contains spectroscopic data of the obtained compounds.

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