Synthesis and Catalytic Activity of N-Heterocyclic Carbene Copper Catalysts Supported on Magnetic Nanoparticles

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Abstract : Carbenes - species which possess neutral carbon atom with two shared and two unshared valence electrons, are known for their high reactivity and instability. Nevertheless, it is also known, that some carbenes i.e. N-heterocyclic carbenes (NHCs), can form stable crystals. The usability of NHCs in organic synthesis was studied. Due to their exceptional properties (high nucleophilicity) NHCs are commonly used as organocatalysts and also as ligands in transition metal complexes. NHC ligands possess better electron-donating properties than phosphines. Moreover, they exhibit lower toxicity. Due to these features, phosphines are frequently replaced by NHC ligands. In this research is discussed the synthesis of five-membered NHCs which are mainly obtained by deprotonation of azolium salts, e.g., imidazolium or imidazolinium salts. Some of them are immobilized on a solid support what leads to formation of heterogeneous, recyclable catalysts. Magnetic nanoparticles (MNPs) are often used as a solid support for catalysts. MNPs can be easily separated from the reaction mixture using an external magnetic field. Due to their low size and high surface to volume ratio, they are a good choice for immobilization of catalysts. Herein is presented synthesis of N-heterocyclic carbene copper complexes directly on the surface of magnetic nanoparticles. Formation of four different catalysts is discussed. They vary in copper oxidation state (Cu(I) and Cu(II)) and structure of NHC ligand. Catalysts were tested in Huisgen reaction, a type of copper catalyzed azide-alkyne cycloaddition (CuAAC) reaction. Huisgen reaction represents one of the few universal and highly efficient reactions in which 1,2,3-triazoles can be obtained. The catalytic activity of all synthesized catalysts was compared with activity of commercially available ones. Different reaction conditions (solvent, temperature, the addition of reductant) and reusability of the obtained catalysts were investigated and are discussed. The project was financially supported by National Science Centre, Poland, grant no. 2016/21/N/ST5/01316. Analyses were performed in Centre of Synthesis and Analyses BioNanoTechno of University of Bialystok. The equipment in the Centre of Synthesis and Analysis BioNanoTechno of University of Bialystok was funded by EU, as a part of the Operational Program Development of Eastern Poland 2007-2013, project: POPW.01.03.00-20-034/09-00 and POPW.01.03.00-20-004/11.

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