

## Abstract

Since the discovery of copper(I) catalysed cycloaddition between organic azides and alkynes into 1,4-disubstituted-1,2,3-triazoles, frequently referred to as click triazoles, these scaffolds have become intensively studied in various fields of chemistry. We synthesized four different series of click triazoles that can serve as N,N-bidentate ligands for a variety of transition metal ions. A selected series of 1,2,3-triazoles, tethered to pyridine, pyrazine and pyrimidine rings was coordinated to ruthenium(II).

In the last decade 1,3,4-trisubstituted triazolium salts have emerged as an interesting subclass of nitrogen heterocycles. These salts found applications in different fields of chemical and material sciences. The most prominent is their use as precursors for abnormal *N*-heterocyclic carbene ligands (*trzNHC*). Triazolium salts can be easily accessed by N-3 alkylation of the 1,2,3-triazole. This is no longer the case when the click triazole is functionalized with potentially reactive nucleophilic group, such as pyridine ring, which can also interfere with the alkylating reagent. Thus, often a mixture of mono- and poly-alkylated non-desired side products is formed. In this context, we recently developed a simple approach to pyridine functionalized click triazolium salts, which is based on selective pyridine ring protection through pyridine-*N*-oxide. We transformed the four series of click triazoles into their triazolium salts. These salts can offer a C,N-bidentate coordination. Thus, we coordinated them to ruthenium(II), iridium(III), osmium(II) and copper(I).

The coordination of click triazoles, as well as triazolium salts was followed by multinuclear NMR spectroscopy. Additionally, the solid-state structures of selected complexes were confirmed by single-crystal X-ray diffraction analyses.

Complexes were tested as catalysts for several transformations, such as direct *ortho*-arylation *via* C–H activation, oxidation of primary and secondary alcohols with *tert*-butyl hydroperoxide (TBHP) in water and transfer hydrogenation catalysis. The electronic effects of the ligands as well as different substrates were investigated. Furthermore some mechanistic elucidations are presented. Selected triazolium salts were tested as precursors for *in situ* formation of the catalysts for the Suzuki-Miyaura coupling.

**Keywords:** click triazoles, triazolium salts, coordination complexes, catalysis.