UNCOMMON REACTIVITY OF THE PROPARGYLAMINE AND PROPARGYLAMIDE SUBSTITUENTS IN THE FUNCTIONALIZED CLATHROCHELATE IRON(II) COMPLEXES

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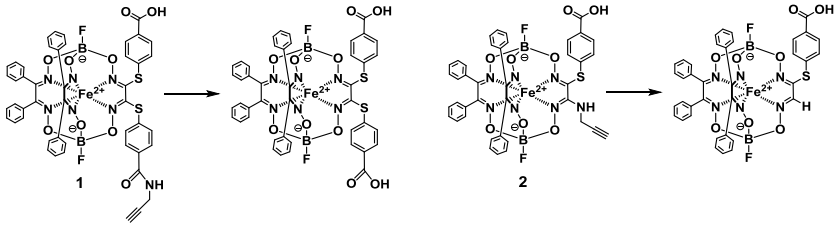
Nowadays, the compounds with ethynyl group(s) are frequently used for their further modifications using the methods of modern so-called “click”-chemistry, based on the metal-promoted 1,3-dipolar cycloaddition reactions. We performed an attempt to obtain new monoribbed-difunctionalized clathrochelate iron(II) complexes with propargylamine- or propargylamide-terminated ribbed substituents as the prospective macrobicyclic precursors of their Sonogashira reactions. However, we observed an uncommon low chemical stability of these propargylamine and propargylamide cage complexes under basic conditions. In particular, the propargylamide substituent of the iron(II) complex **1** (Scheme) underwent a slow hydrolysis in the presence of triethylamine in its dichloromethane solution, thus giving the terminal carboxyl group, while, in the case, of the clathrochelate **2**, its reductive elimination reaction occurred. The same result was observed after a stirring of the dichloromethane solution of this monopropargylamine iron(II) cage complex with $NaHCO_3$ aqueous solution.



Scheme

As follows from MALDI-TOF mass-spectrometry data, our attemps to modify the clathrochelate **1** using its Sonogashira reaction gave only the traces of the target macrobicyclic product. We suggest that its terminal propargylamine group undergoes a hydrolysis in the presence of the corresponding Hunig base rather than the corresponding Sonogashira reaction. At the moment, we are under way to perform an optimization the conditions of the latter C–C cross-coupling reaction, trying to increase its yield.

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