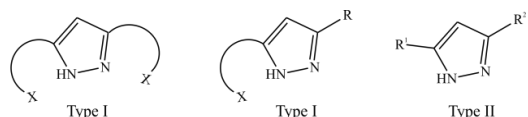


Homo- i heterometaliczne metalamakrocycliczne układy cynkowe otrzymane przez transformacje cynkoorganicznych kompleksów pirazoli RZnPz

Metallamacrocycles (MMCs) are cyclic metal-organic clusters comprising of metal ions bridged by organic and sometimes inorganic ligands. Such a broad definition covers a wide range of structurally varied compounds, including metallacrowns (MCs), metallocryptates, metallocavitands, molecular rings and more. The extensive attention attracted by MMCs stems not only from their esthetic appeal, but also because of the wide range of potential applications including: sensors, catalysts, advanced magnetic materials, building units for extended solids, ion and small molecule recognition agents. Among successful ligands for constructing MMC compounds are derivatives of 1H-pyrazole (denoted as HPz). Upon deprotonation HPz are converted into monoanionic pyrazolate anions, which feature a Lewis basic N-N motif, that facilitates formation of polynuclear metal systems. To date, many fascinating metal pyrazolate compounds were reported, many with metallamacrocyclic architectures. In this context, it is surprising to find, that there are only 4 zinc pyrazolate MMCs.¹ The planned research will result in changing this situation, by developing highly efficient methods for preparation of zinc pyrazolate MMCs through transformations of well defined organozinc pyrazolates (RZnPz) in presence of O₂ and H₂O. The literature shows a relative paucity concerning the

structural characterization of the latter compounds, as well as the products of their hydrolysis and oxygenation. Until recently, only type I organozinc pyrazolates with



X = donor centers - e.g. N, S, O
R = alkyl, aryl, H

Figure 2. A schematic representation of types of 1H-pyrazole derivatives, based on the type of 3- and 5-substituent

dinuclear structures were reported.

The situation changed this year, when fascinating results on the structural diversity of type II organozinc pyrazolates were published by prof. Lewiński. These intriguing findings have provided new opportunities

for this type of compounds as precursors of functional [ROZnPz] (R = O-alkyl, alkyl, aryl or H) type based materials.

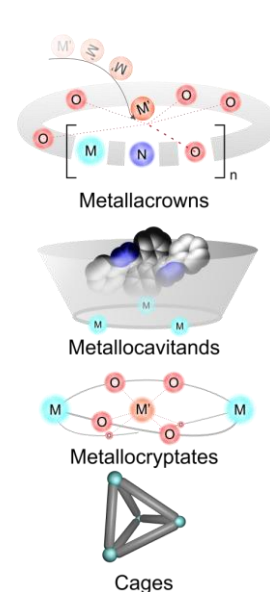


Figure 1. Schematic representation of various kinds of MMCs

Lewiński group has a long history of comprehensive research on the reactivity of organozinc reagents towards O₂. Back in the old days, the idea of controlling the oxygenation of highly flammable zinc organometallics was deemed unbelievable. In spite of that, the systematic approach to this problem proven, that in proper conditions these processes can in fact be controlled and selective formation of zinc alkylperoxide may take place. What is more, further investigation has led to the development of a plausible mechanism explaining this phenomenon, allowing for the design of new reaction systems for rational synthesis of zinc alkylperoxide materials with exceptional catalytic properties in epoxidation of enones

A comparable challenge in the field of organozinc chemistry is harnessing the hydrolysis process. This reaction may lead to the highly desired from the view of materials chemistry oxo- and hydroxyzinc clusters. Regardless, the transformations of organozinc systems in presence of water have not been systematically investigated. A significant amount of structurally characterized products of these reactions was obtained serendipitously (e.g. upon unintended introduction of small amounts of air or insufficient drying of solvents), and only in single cases the products are isolated with good yields. The controlled hydrolysis of RZnL compounds is particularly challenging, since both the zinc bonded alkyl group as well as the ligand can be cleaved.

The highly original approach towards the synthesis of homometallic zinc pyrazolate MMCs based on the transformations of well-defined organozinc pyrazolate compounds should open the access to previously unavailable zinc MMCs. An integral part of the project will include investigating the properties of these compounds, including their affinity towards complexing other metal cations and in this way providing new heterometallic assemblies. Moreover, the proposed research should allow to significantly broaden the current state of knowledge concerning the controlled hydrolysis of organozinc compounds. Finally, a variety of novel [RZnPz]-type compounds will be obtained and the factors determining their structure scrutinized.

¹ Based on the information derived from the CCDC v2016