FACULTY OF SCIENCE
Charles University

Department of

Inorganic Chemistry

**PhD thesis report**

Thesis Title: Synthesis and Application of Transition Metal Complexes Bearing *N*-Heterocyclic Carbene Ligands

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The thesis by Miguel Alexandre Gomes Mateus is structured into three major sections: Introduction, Results and Discussion, and Experimental Section. The primary focus of the dissertation is on the synthesis, characterization, and application of transition metal complexes with polydentate *N*-heterocyclic carbene (NHC) ligands, particularly silver complexes. The work explores the synthesis of these complexes, their potential as catalysts, antimicrobial agents, and their novel application in data storage.

The literature section provides a comprehensive overview of *N*-heterocyclic carbenes (NHCs), highlighting their discovery, electronic properties, and their role in stabilizing transition metal complexes (NHCs are explored mostly for their strong σ-donating ability, which makes them valuable ligands in various catalytic and medicinal applications). The author discusses the synthetic methods and structural diversity of NHC-silver(I) complexes. Emphasis is placed on their ease of synthesis, stability, and the variety of binding motifs that these complexes can exhibit. A significant portion of the review is dedicated to the transmetalation process, where NHC ligands are transferred from silver complexes to other transition metals such as nickel and palladium. This process is crucial for expanding the scope of metal-NHC complexes. The literature also covers the concept of chirality in metal complexes, which arises from the coordination of achiral ligands to metal centers, leading to chiral-at-metal complexes. The literature review is thorough and well-structured, providing a solid foundation for the experimental work. It effectively connects historical developments in NHC chemistry with the current research focus, offering a clear rationale for the choice of research topics. All aspects of the chemistry of carbene ligands and their complexes discussed in the introduction of the thesis facilitate orientation in the rather extensive

experimental part of the thesis, where the studied substances are used in several widely ranging areas from catalysis, through medical applications to the use in data storage.

The actual experimental work described in this thesis aims at the synthesis of polydentate NHC ligands based on the bis(carboxamide) backbone and their subsequent coordination with silver(I). The author successfully synthesized not only simple mononuclear NHC-silver(I) complexes, but he was able to isolate even interesting polynuclear species with intriguing structure. Besides, the transmetalation of NHC ligands from silver to other transition metals such as nickel and palladium was explored. The resulting complexes were found to exhibit chirality due to the coordination of the ligand in a helical manner.

The antimicrobial activity of the synthesized silver complexes was evaluated against a range of microorganisms, including gram-positive and gram-negative bacteria, as well as fungi. The complexes demonstrated interesting antimicrobial properties, with minimum inhibitory concentrations (MIC) as low as 1 μg/ml. Further, the silver complexes were tested as catalysts in multicomponent coupling reactions such as A3 (aldehyde, amine, alkyne) and KA2 (ketone, amine, alkyne) couplings. The complexes showed high catalytic activity, yielding products with excellent overall yields and broad substrate scope tolerance. Finally, a novel application of the compounds synthesized readily by the described multicomponent catalytic reaction was explored in data storage, a field that remains relatively unexplored.

In summary, the author has done a significant amount of experimental work and has managed to present it in his dissertation in a comprehensive way. The synthesized polydentate *N*-heterocyclic carbene ligands based on the carboxamide backbone and their complexes are versatile in their applications, ranging from antimicrobial agents to useful catalysts. The work therefore represents a useful contribution to the coordination chemistry of silver(I) (the part dedicated to other metals remains rather minor). The overall quality of the thesis is confirmed by the fact that the work on catalysis and antimicrobial activity has already been successfully published. Although the author failed to avoid common mistakes such as typos (R-xay on the page 47), numbering errors (the most severe errors that I have found in this thesis are erroneous numbering of compounds in Schemes 28 and 30 and in the accompanying text), inconsistent formatting (for instance frequently missing bold in compounds numbering) or wrong terminology (complex **23** is definitely not chelating), these errors are not so frequent as to detract severely from the quality of the work. I can therefore recommend it for acceptance as a qualifying thesis for the PhD degree.

Questions and remarks:

1) You have studied the conformational switch of nickel and palladium complexes **110** and **111**. Two pathways have been suggested based on the obtained NMR data and performed DFT calculations. Have you also considered possibility, that the conformational switch proceeds through abnormal carbene intermediate (as mentioned for some Pd complexes with similar ligands in the section 4.2.1.)?

2) You have prepared some chiral at metal complexes and you attempted also synthesis of chiral ligand to combine helical and point chirality. Did you think about synthesizing carboxamides derived from 1,2-diaminocyclohexane? You suggested it as structure **84**. Such a ligand would be a carbene analogue of famous (and in asymmetric catalysis very successful) Trost ligand.

3) Polydentate amido-carbene ligands are frequently used in stabilization of high valent transition metal complexes (Fe for instance), that could be used for instance for C-H activation. Did you try transmetalation to such a type of high valent transition metal ions? (I know that you have tried low valent Fe, Co and Mn).

4) You have explored the prepared complexes in various applications. However, (NHC)-silver(I) complexes exert frequently also interesting luminescent properties – especially polynuclear complexes such as the complex **108**. Have you tried luminescent behaviour of your compounds (at least by a simple laboratory UV lamp)?

5) Considering polynuclear silver(I) complexes – their solid-state structures are frequently influenced to various extent by argentophilic interactions (similar type of non-covalent interactions such as the better known aurophilic interaction). Have you observed them (either intramolecular or intermolecular) in the crystal structure of the complex **108**? Or in the crystal structures of your other complexes?

6) When discussing conformation of nickel and palladium complexes **110** and **111**, you have mentioned distortion angle. Tetrahedral distortion of square-planar complexes can be easily quantified by geometry parameter $\tau_4$ (this parameter helps to distinguish between square-planar and tetrahedral complexes). Could you calculate it for the complexes from the Figure 20 and compare it with the conclusions based on the calculated distortion angles?

Prague, August 23, 2024

RNDr. Jiří Schulz, Ph.D.