

1. PhD PROJECT DESCRIPTION (4000 characters max., including the aims and work plan)

Project title:

Mechanistic clarification of the interaction of nanoscale coordination compounds at the interface of multiphase chemical processes

1.1. Project goals

-To investigate the modification of NSCC (in the solid state) via the interaction with strong nucleophiles (in solution) to induce typical ligand substitution and redox reactions within the coordination sphere of the NSCC.

-To investigate the role of homogeneous-heterogeneous interactions that can contribute to the efficiency of such reactions through a systematic variation of reaction conditions in terms of temperature, pH, ultrasound and solvent effects.

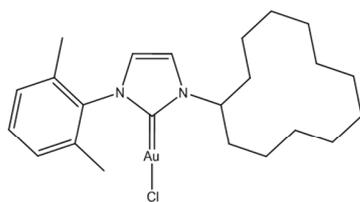
-To contribute to the mechanistic clarification of multiphase ligand substitution reactions and their ability to affect the redox potential of NSCC in applications dealing with redox cell biology.

1.2. Outline

The mechanistic understanding of chemical reactions at the solid-liquid interface of chemical processes involving nanoscale coordination compounds (NSCC), has received little experimental attention and is mostly described by computational techniques.¹ Such knowledge is crucial to understand the advantages and disadvantages of NSCC. As far as we know, such processes have not been investigated in detail for NSCC before. In a recent study,² as proof of principle, we demonstrated the efficiency of ligand substitution reactions at the solid-liquid interface of a submicron Au(I) carbene complex using an anti-solvent technique. A reproducible method was developed with which submicron particles of an Au(I) NSCC can undergo ligand substitution reactions at the solid-liquid interface of a multiphase chemical reaction. The resulting particles were analyzed by a combination of SEM, DLS and EDX spectroscopy in the solid state, and their optical properties by UV/Vis spectroscopy in ethanol solution. In this model system the chlorido ligand of the Au(I) complex in the solid state was systematically displaced by iodide from the surrounding solvent in which the submicron particles were insoluble.

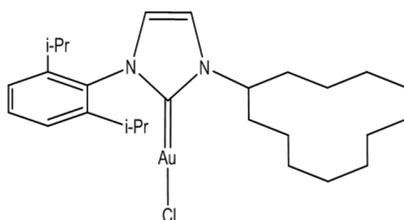
1.3. Work plan

-The reactions of complex **1** were investigated for the entering nucleophiles KI, NEt₄I, Na₂S, thiourea and NaCN.² The series will now be extended to complexes **2** and **3** to determine the effect of the alkane back-bone on the overall reactivity of the carbene complexes in reactions with the series of nucleophiles quoted above.



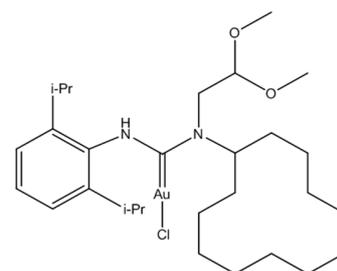
Molecular Weight: 570,96

1



Molecular Weight: 627,06

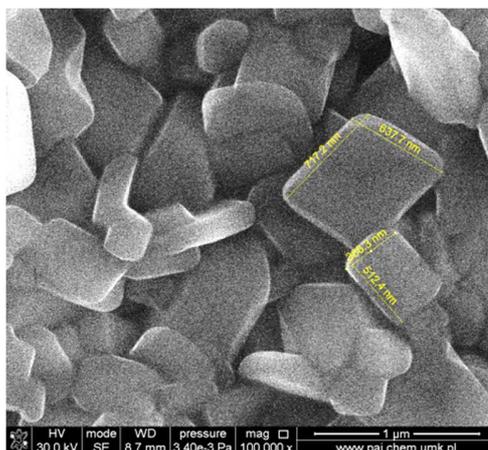
2



Molecular Weight: 691,15

3

-A systematic study of ligand substitution reactions on NSCC of Ru(II)-polypyridyl complexes will be undertaken as a function of the anti-solvent, sonication time, nucleophilicity and concentration of the entering ligand, surfactant type and concentration, pH, temperature and reaction time. Preliminary results showed that such NSCC can indeed be formed in the case of $[\text{Ru}^{\text{II}}(\text{terpy})(\text{bipy})\text{Cl}]\text{Cl}$:



NSCC of $[\text{Ru}^{\text{II}}(\text{terpy})(\text{bipy})\text{Cl}]\text{Cl}$

-The activation of small molecules such as O_2 , CO_2 , NO and H_2O_2 , i.e. processes that are of fundamental interest to biology,³ will be studied with the application of NSCC of Fe(III) and Co(III) porphyrin complexes.

-Finally, redox reactions of NSCC of Ru(III) will be studied with suitable redox partners based on our earlier work in homogeneous solution.⁴

Such systematic studies will enable us to gain more insight into the mechanism of ligand substitution and electron transfer reactions at the solid-liquid interface of chemical processes.

1.4. Literature

1. J.R. Rustad, W.H. Casey, *Nature Mat.*, 11, 223-225 (2012). W.H. Casey, *Environm.*

Chem.12, 1-19 (2015). W.H. Casey, Adv. Inorg. Chem., 69, 91-114 (2017).

2. D. Langford, M. Djurovic, M. Oszejca, J. Kuncewicz, R. van Eldik, Angew. Chem. Int. Ed., 57, 663-667 (2018).

3. A. Franke, R. van Eldik, Chem. Eur. J., 21, 15201-15210 (2015). M. Oszejca, A. Franke, M. Brindell, G. Stochel, R. van Eldik, Coord. Chem. Rev., 306, 483-509 (2016).

4. O. Impert, A. Katafias, J. Fenska, M. Chrzanowska, S. Koter, C. Dücker-Benfer, R. van Eldik, Eur. J. Inorg. Chem., 5380–5386 (2016). M. Chrzanowska, A. Katafias, O. Impert, A. Kozakiewicz, A. Surdykowski, P. Brzozowska, A. Franke, A. Zahl, R. Puchta, R. van Eldik, Dalton Trans., 46, 10264–10280 (2017).

1.5. Required initial knowledge and skills of the PhD candidate

- Basic understanding of transition metal coordination chemistry
- Basic understanding of reaction kinetics in solution
- Keen to learn new techniques and instrumentation
- Eager to work hard and contribute to the success of the project
- Keen to be part of a dynamic research team

1.6. Expected development of the PhD candidate's knowledge and skills

The candidate will receive a basic training in the following knowledge and skills:

- Detailed understanding of the complexity of solid-liquid interactions at the interface of solid submicron coordination complexes in solution.
- The application of a variety of spectroscopic techniques such as SEM, DLS and EDX spectroscopy in the solid state, and optical properties by UV/Vis and NIR spectroscopy in solution.
- Clarification of the underlying reaction mechanisms of ligand substitution processes in the solid state at the interface of the solid-liquid system.
- Presentation of the candidate's results at group meetings and at local and international meetings in the form of poster and oral presentations.