

**Synthesis and isolation of previously infeasible dithiolato bridged dinuclear ruthenium complexes  $[(p\text{-MeC}_6\text{H}_4i\text{Pr})_2\text{Ru}_2\text{SR}_2\text{Cl}_2]$  using optimized reaction conditions**H. Primasova<sup>1</sup>, M. De Capitani<sup>1</sup>, I. Gjuroski<sup>1</sup>, J. Furrer<sup>1\*</sup><sup>1</sup>Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland

It is well known that the dimer *p*-cymene-ruthenium dichloride  $[(p\text{-MeC}_6\text{H}_4i\text{Pr})_2\text{Ru}_2(\text{m-Cl})_2\text{Cl}_2]$  reacts with aromatic thiols to give cationic trithiolato complexes  $[(p\text{-MeC}_6\text{H}_4i\text{Pr})_2\text{Ru}_2(\text{SR})_3]^+$  [1]. The reaction proceeds through neutral dithiolato intermediates  $[(p\text{-MeC}_6\text{H}_4i\text{Pr})_2\text{Ru}_2(\text{SR})_2\text{Cl}_2]$ , some of which could be isolated in good yields [2]. From our previous studies, a prerequisite for the successful isolation of dithiolato intermediates was that the thiol must be aliphatic, otherwise the reaction cannot be controlled and leads immediately to the corresponding cationic trithiolato complexes [3].

Herein, we report the synthesis of new dithiolato complexes  $[(p\text{-MeC}_6\text{H}_4i\text{Pr})_2\text{Ru}_2(\text{SR})_2\text{Cl}_2]$  with aromatic thiols (R=*p*-*t*-Bu-Ph: **1**; *p*-MeO-Ph: **2**; *p*-Br-Ph: **3**) in good to excellent yields and sufficient level of purity for **1** and **2**. The complexes could be obtained using optimized conditions (DCM, 4h, 0-25°C).

Despite being generally biologically less active than their corresponding trithiolato counterparts, dithiolato intermediates can be further functionalized with a different thiol, R<sup>2</sup>, giving a mixed trithiolato complexes  $[(p\text{-MeC}_6\text{H}_4i\text{Pr})_2\text{Ru}_2(\text{SR}^2)(\text{SR})_2]^+$  which are known to be highly cytotoxic against cancer cells [4]. Depending on the nature of R<sup>2</sup>, the complexes can be further functionalized with bioactive molecules, thus strongly increasing the chemical variability and the bioactivity of the complexes [5]. As such, the present work represents the first step of our general goal which is to synthesize numerous new ruthenium conjugates with different properties.

[1] J. Furrer and G. Süss-Fink, *Coord. Chem. Rev.*, **2016**, 309, 36-50.

[2] A.-F. Ibaño, M. Gras, B. Therrien, G. Süss-Fink, O. Zava, and P. J. Dyson, *Eur. J. Inorg. Chem.*, **2012**, 2, 1531-1535.

[3] M. A. Furrer, A. Garci, E. Denoyelle-Di-Muro, P. Trouillas, F. Giannini, J. Furrer, C. M. Clavel, P. J. Dyson, G. Süss-Fink, and B. Therrien, **2013**, *Chem. - A Eur. J.*, 19, 3198-3203.

[4] F. Giannini, J. Furrer, G. Süss-Fink, C.M. Clavel, P.J. Dyson, *J. Organomet. Chem.*, **2013**, 744, 41-48.

[5] F. Giannini, M. Bartoloni, L.E.H. Paul, G. Süss-Fink, J.-L. Reymond, J. Furrer, *MedChemComm*, **2015**, 6, 347-350.