## Synthesis and isolation of previously infeasible dithiolato bridged dinuclear ruthenium complexes [( $p-MeC_6H_4iPr$ )<sub>2</sub>Ru<sub>2</sub>SR<sub>2</sub>Cl<sub>2</sub>] using optimized reaction conditions

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It is well known that the dimer *p*-cymene-ruthenium dichloride  $[(p-MeC_6H_4iPr)_2Ru_2(m-Cl)_2Cl_2]$  reacts with aromatic thiols to give cationic trithiolato complexes  $[(p-MeC_6H_4iPr)_2Ru_2(SR)_3]^+$  [1]. The reaction proceeds through neutral dithiolato intermediates  $[(p-MeC_6H_4iPr)_2Ru_2(SR)_2Cl_2]$ , some of which could be isolated in good yields [2]. From our previous studies, a perquisite 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  $[(p-MeC_6H_4iPr)_2Ru_2(SR)_2Cl_2]$  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 then their corresponding trithiolato counterparts, dithiolato intermediates can be further functionalized with a different thiol,  $R^2$ , giving a mixed trithiolato complexes  $[(p-MeC_6H_4iPr)_2Ru_2(SR^2)(SR)_2]^+$  which are known to be highly cytotoxic against cancer cells [4]. Depending on the nature of  $R^2$ , 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. Ibao, M. Gras, B. Therrien, G. Suess-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. Suss-Fink, C.M. Clavel, P.J. Dyson, J. Organomet. Chem., 2013, 744, 41-48.

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