

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 conditionsH. Primasova¹, M. De Capitani¹, I. Gjurroski¹, J. Furrer^{1*}¹Departement 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, R², 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 R², 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.

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