Synthesis and isolation of previously infeasible dithiolato bridged dinuclear ruthenium complexes [(p-$MeC_6H_4iPr)_2Ru_2SR_2Cl_2$] using optimized reaction conditions

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It is well known that the dimer *p*-cymene-ruthenium dichloride [(*p*-$MeC_6H_4iPr)_2Ru_2(m\text{-}Cl)_2Cl_2$] 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.

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