Optimized reaction conditions for the synthesis of trithiolato-bridged dinuclear arene ruthenium complexes: reducing the reaction time and synthesis of new complexes

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Trithiolato-bridged dinuclear arene ruthenium complexes $[(\text{arene})_2\text{Ru}_2(\text{SR})_3]^+$ can be obtained using a very simple and efficient method (complexes are obtained in yields larger than 80%), using a refluxed solution of thiols dissolved in ethanol taking advantage of the remarkable preference for the SH function versus the OH function of the solvent by the dinuclear ruthenium unit [1]. Depending on the reactivity of the thiol, very good yields are typically obtained within 12 to 48 h [2]. We have however noticed that some of those trithiolato-bridged dinuclear arene ruthenium complexes were difficult to obtain.

In this contribution, our idea is to use organic bases to increase the reactivity of the thiols in order to reduce the overall reaction time and to synthesize trithiolato-bridged dinuclear arene ruthenium complexes that were difficult to obtain by the classical method. For this, three known diruthenium trithiolato complexes $[(p\text{-MeC}_6\text{H}_4{}^i\text{Pr})_2\text{Ru}_2(\text{SR})_3]^+$ (R=p-^{t}BuPh :**1**, p-MeOPh :**2**; p-BrPh :**3**) were synthesized using various reaction conditions. Under optimized conditions (dichlormethane in presence of N,N-diisopropylamine under reflux) **1** could be obtained in as short as two hours with quantitative yield. These optimized reaction conditions were implemented for **2** and **3**, with 96% and 87% yield, respectively, in as less as 2 h as well, compared to 24 h using the classical method. [2] Finally, using the optimized reaction conditions applied for 70 h, complex with R=$\text{CH}_3(\text{CH}_2)_5$:**4**, related to the previously reported complex with R=$(\text{CH}_2)_7\text{CH}_3$ obtained in 7 days in yield of 28% [3] , could be prepared and isolated in good yield of 68%.

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