

Electronic Supplementary Information for

Intramolecular communication and electrochemical observation of the 17-electron ruthenocenium cation in fluorinated ruthenocene-containing β -diketones; polymorphism of $C_{10}H_{21}$ and $C_{10}F_{21}$ derivatives

Elizabeth Erasmus and Jannie C. Swarts*

Supplementary information for paragraph 3.4. Keto-enol Isomerisation Kinetics

In principle two enol isomers can exist in equilibrium ($Rc-C(OH)-CH-CO-R \rightleftharpoons Rc-CO-CH-C(OH)-R$). However, in practice only one set of enol tautomer signals is observed on the NMR. This implies that either the conversion from one enol tautomer to the other is fast on the NMR time scale, or that only one tautomer exist. Either way, upon interpreting NMR spectra of the enol tautomers, the measured integral values of the enol tautomers would be indicative of the total enol tautomers content in solution.

A comparison of the rates of isomerisation in CD_3CN , (Table 2 main text), shows that the long chain alkyl R-group $C_{10}H_{21}$ (**4**) isomerises the slowest and that the two new β -diketones having fluorinated R-groups $C_{10}F_{21}$ (**1**) and C_6F_5 (**3**) isomerises slightly faster than the CF_3 (**2**). In both solvents compound **4** with $R = C_{10}H_{21}$ isomerised the slowest and **7** with $R =$ ruthenocetyl isomerised the fastest. However, the ratio between the slowest and the fastest half-lives is for $CDCl_3$ $49856/220 = 226$ but for CD_3CN it is only $18381/4620 = 4$; this is a difference of two orders of magnitude.

Assessing the data of **1-8** in Table 2 (main text) in both CD₃CN and CDCl₃ revealed that the enol isomer is more abundant for **2, 3, 4** and **7** in CD₃CN than in CDCl₃, but for **1, 5, 6** and **8** the keto isomer is most abundant at equilibrium. With the exception of **2** and **4** the equilibrium constants, K_c, and the k_{obs} rate constants are larger in CDCl₃ than in CD₃CN.

Supplementary information for paragraph 3.5, Electrochemistry

Equation 8 was determined to estimate the redox properties of the R_c group in ruthenocene-containing β-diketones.

$$E_{\text{pa}} = 270.91\chi_{\text{R}} + 228.2; R^2 = 0.8964 \quad (8)$$

Ideally one would prefer to relate the formal oxidation potential $E^{\circ} = (E_{\text{pa}} + E_{\text{pc}})/2$ with χ_{R} because E° is a thermodynamic quantity while E_{pa} is not. However, because wave 3 corresponding to E_{pc} were not detected for all compounds in the compound series **1 – 8**, a relationship based on E° could not be established.